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SOIL SCIENCE

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THE LIME FACTOR IN PERMANENT SOIL IMPROVEMENT

I. Rotations Without Legumes

J. G. LIPMAN and A. W. BLAIR

New Jersey Agricultural Experiment Station

Received for publication January 1, 1920

The fact that lime in one or another of its forms has a distinct value in the production of many crops, and in improving the physical character of certain types of soil, which in the end means improved crops, has long been known. Thus for centuries lime materials have been used in almost every country and for practically all crops. Various writers have laid special emphasis on the natural fertility of limestone soils; that is, soils having a high percentage of carbonate of lime; and the expression that "a lime country is a rich country" has come to be rather widely accepted. Very much has been written concerning the reasons for the beneficial effects of lime on crop production, but it is probably safe to say that, in the majority of cases, its use has been on general principles rather than as a result of the careful searching out of the reasons for its effectiveness.

It is well known that its use affects some crops more than others, and that some soils are more responsive than others.

Anyone who is at all familiar with the subject has heard the expression, "Lime makes the father rich and the son poor," the meaning of which, no doubt, was that lime aids in "mining" the soil rather than in permanently building it up.

We now know that the words quoted do not necessarily express the facts. Much depends on how the lime is used, and the system of cropping followed, as to whether the son will be poorer or richer than the father.

A quarter of a century ago, little was known as to the influence of lime on soil organisms, whereas we now know that it plays a very important part in this respect.

It has been shown, for example, that there were many more nodules on the roots of soybeans grown on limed plots than on unlimed plots (4, 5), and that both the beans and stalks from limed plots were richer in nitrogen than those from unlimed plots. This perhaps may not be held to be positive proof that lime favors the development of the symbiotic organisms, and that these organisms in turn enable the plant to store up more nitrogen than plants on the unlimed plot; but it is about as near the positive proof as we can come with our present state of knowledge. Certainly, for the practical man, the proof is sufficient.

It has been shown also that, for a period of years, the percentage of nitrogen was higher in alfalfa hay from limed than from unlimed plots, and that, for this period of years, far more total nitrogen was secured in the hay from the former than from the latter (3). Here again, we are lacking the positive direct proof of the beneficial influence of lime on symbiotic organisms, but the indirect proof is at least something to hold to until more direct proof can be secured.

It is now well known that organic matter in the soil, such as crop residues and farm manures, is converted into new plant-food more rapidly on soils that are well supplied with carbonate of lime than on soils that have an acid nature. This is explained on the ground that the organisms which cause the breaking down of the organic matter, with the consequent formation of available nitrogen compounds, find the soil containing the lime carbonate, a more favorable medium for work than the acid soil. Thus it comes about that, other limiting factors being overcome, larger crops, or crops containing a higher percentage of nitrogen, or both, are often produced on soils that are abundantly supplied with the carbonate of lime.

It is conceivable, however, that this process may be carried too far; that is, the breaking down of the organic matter may become excessive, with the so-called "burning out" effect. Indeed, it is very evident that, with favorable conditions and a limited supply of organic matter, this must finally happen. In other words, it is clear that there may be soils—especially those of light, open character—having such a limited supply of organic matter as to require the checking influence of a slightly acid condition.

It is quite evident, therefore, from what has been said, that in considering the lime question, very careful attention should be given to the type of soil, the crops to be grown, and the disposition that is to be made of these crops.

It is quite certain that such experiments, to be of value, should be carried on over a considerable period of years, since the composition of the soil as determined by methods of analysis now in use, is seldom very much changed in a shorter period than 5 years.

It is with the hope of bringing into clearer light the reasons for the use of lime in agriculture and especially in its relation to the permanent improvement of soils, that this work, covering a period of 10 years, is reported.

PLAN OF EXPERIMENT

In 1908 a field experiment was laid out having as its object a study of the nitrogen problem in crop production. The plan includes a study of the sources of nitrogen, the proper amount to apply, the influence of nitrogen on the yield and composition of the crop, denitrification and other nitrogen losses; also, on account of the important bearing which the reaction of the soil has on the nitrogen problem, the plan was made to include the use of lime in the carbonate form. For this purpose, two series of plots were laid out with identical fertilizer treatment—but differing in that the 20 plots hereafter

designated as 1A to 20A, were to remain unlimed while the 20 hereafter designated as 1B to 20B were to be limed at stated intervals.

The soil is a Sassafras loam, inclining to a sandy loam, which originally contained 0.11 per cent of nitrogen and 1.22 per cent of total carbon. Lime-requirement determinations were not made at the time the experiment was started, but if we may judge from determinations made on unlimed plots later, it is safe to assume that the lime requirement in 1908 was about 1600 to 2000 pounds of lime (CaO) for 2,000,000 pounds of the soil. As this land had not been under cultivation for a number of years, it is certain that up to 1908, no lime had been applied within recent years.

The plots were laid out $\frac{1}{20}$ acre in size, being about twice as long as wide. The crop rotation, as orginally planned, was: 1 year of corn, 2 years of oats, a year of wheat and one of timothy. This was later changed so that there was 1 year of oats and two of timothy. This is a rotation that was practised more or less some years ago, but would perhaps not be applicable to present conditions.

Since the experiment provides for a study of nitrogenous fertilizer materials, no leguminous crop can be introduced in the rotation, either as one of the main crops or as a green-manure crop. However, it may be noted here that during the summer and fall of 1912, much volunteer clover appeared in the timothy and made considerable growth after the latter had been cut. This clover was later dug out, dried and weighed, and analyzed for nitrogen. The yield of dry matter (clover) from the limed plots was almost double that from the unlimed plots (2). Likewise, samples from the limed plots showed a higher percentage of nitrogen than samples from the unlimed plots.

The lime treatment has consisted of finely ground limestone or oyster shells at the rate of 1 ton per acre just before planting the corn in 1908, and 2 tons per acre again preceding the corn in 1913, the liming thus taking place at intervals of 5 years. A careful record has been kept of the amount of nitrogen applied in the form of manure and fertilizer, and likewise of the amount removed by the crops. Samples of soil were collected for analysis previous to applying the lime in 1913, and again in the fall of 1917.

The manure and fertilizer treatment given these plots, the lime requirement (Veitch method) and the analytical data secured on the soil samples taken at the end of each 5-year period are shown in table 1.

From this table it will be noted that the average lime requirement in 1913 for all of the A plots (unlimed) was 1840 pounds of CaO per acre, and for all the B plots (limed) 1140 pounds. Thus notwithstanding the ton of limestone per acre which was used in 1908, all of the B plots had become quite acid at the end of the first 5 years.

At the end of the second 5 years the average lime requirement for the A plots was 1615 pounds per acre, which is slightly less than the requirement at the end of the first 5 years, although no lime had been applied. On the other hand, the soil of the B plots which had in 1913 received 2 tons of ground

TABLE 1

Lime requirement (Veitch method), total carbon and total nitrogen, 1908–1917

NUMBER	FERTILIZER TREATMENT ($\frac{1}{20}$ ACRE PLOTS)	A'S UNLIMED						B'S LIMED					
		Lime requirement per acre		Total carbon		Total nitrogen		Lime requirement per acre		Total carbon		Total nitrogen	
		First 5 years	Second 5 years	First 5 years	Second 5 years	First 5 years	Second 5 years	First 5 years	Second 5 years	First 5 years	Second 5 years	First 5 years	Second 5 years
		lbs.	*lbs.*	*per cent*	*per cent*	*per cent*	*per cent*	*lbs.*	*lbs.*	*per cent*	*per cent*	*per cent*	*per cent*
1	Nothing	1400	1400	1.39	1.33	0.1059	0.1033	1200	Alk.	1.06	0.90	0.0862	0.0770
2	16 pounds muriate of potash	2100	1600	1.44	1.33	0.1098	0.1173	1000	Alk.	1.14	0.96	0.0871	0.0790
3	32 pounds acid phosphate	2100	1600	1.28	1.24	0.1042	0.1139	1000	200	1.07	0.86	0.0821	0.0751
4	Minerals only*	2100	2000	1.36	1.26	0.1180	0.1088	1100	400	1.15	1.04	0.0855	0.0779
5	Minerals and 1600 pounds cow manure	2100	1800	1.38	1.44	0.1002	0.1185	1200	Alk.	1.44	1.42	0.1030	0.1143
6	Minerals and 1600 pounds horse manure	2200	2700	1.39	1.57	0.0929	0.1230	1500	600	1.43	1.48	0.1028	0.1190
7	Nothing	1600	1000	0.95	0.93	0.0790	0.0785	1000	Alk.	1.17	1.02	0.0879	0.0821
8	Minerals and 8 pounds $NaNO_3$	1400	1600	1.11	1.03	0.0880	0.0883	1100	200	1.08	1.01	0.0801	0.0787
9	Minerals and 16 pounds $NaNO_3$	2100	1000	1.15	1.13	0.0921	0.0975	1000	200	1.08	0.96	0.0753	0.0810
10	Minerals and $Ca(NO_3)_2$ equivalent to 16 pounds $NaNO_3$	2100	1000	1.14	1.10	0.0941	0.0903	1200	Alk.	1.12	1.01	0.0805	0.0779
11	Minerals and $(NH_4)_2SO_4$ equivalent to 16 pounds $NaNO_3$	2100	2000	1.14	1.21	0.0977	0.0904	1500	1000	1.02	1.06	0.0801	0.0819
12	Minerals and $CaCN_2$ equivalent to 16 pounds $NaNO_3$	1400	1000	1.03	1.02	0.0869	0.0844	1000	200	1.16	1.07	0.0861	0.0896
13	Minerals and dried blood equivalent to 16 pounds $NaNO_3$	2100	1800	1.14	1.23	0.0925	0.1063	1100	600	1.05	0.98	0.0807	0.0826
14	Minerals and dried fish equivalent to 16 pounds $NaNO_3$	2100	1800	1.26	1.22	0.1014	0.1058	1100	400	1.08	0.93	0.0779	0.0889
15	Minerals and tankage equivalent to 16 pounds $NaNO_3$	1800	1600	1.21	1.18	0.0884	0.0919	1200	Alk.	0.93	0.89	0.0717	0.0803
16	Minerals and 200 pounds alfalfa hay (cut fine)	2100	1600	1.20	1.14	0.0891	0.1012	1100	1000	1.18	1.10	0.0897	0.0904
17	Minerals and 200 pounds rye straw (cut fine)	1600	1600	1.26	1.08	0.0950	0.0980	1100	Alk.	1.25	1.15	0.0953	0.0952
18	Minerals and 1600 pounds cow manure plus 16 pounds $NaNO_3$	1600	2000	1.47	1.36	0.1088	0.1171	1200	Alk.	1.41	1.48	0.1014	0.1190
19	Minerals only	1400	1600	1.29	1.01	0.0980	0.0872	1100	Alk.	1.11	0.95	0.0809	0.0784
20	Minerals and 200 pounds rye straw plus 16 pounds $NaNO_3$	1400	1600	1.23	1.03	0.0959	0.0908	1100	Alk.	1.14	1.12	0.0832	0.0903
	Average	1840	1615	1.24	1.19	0.0969	0.1006	1140	240	1.15	1.07	0.0859	0.0879

* 32 pounds acid phosphate and 16 pounds muriate of potash.

limestone per acre showed either an alkaline or only a slight acid condition in 1917.

No satisfactory explanation appears for the less acid condition of the A plots in 1917 than in 1913. It is conceivable that such a change might be brought about by the oxidation of organic acids resulting from careful and thorough cultural methods.

Of more interest, perhaps, is a comparison of the percentage of nitrogen and carbon in the soil from the two series of plots. The results are shown in table 1 along with the lime-requirement determinations. A study of the averages shows that there is distinctly less of both carbon and nitrogen in the soils of the limed series than in those of the unlimed series. These averages represent 20 plots in each series, and cover a period of 10 years. The fertilizer treatment which the plots have received is indicated in the table. The majority of the plots have received applications of nitrogenous fertilizers somewhat in excess of general practice; a few have received excessive amounts, while a few others have received no nitrogen at all.

TABLE 2

Average percentage of total nitrogen and carbon in limed and unlimed series at different times

	TOTAL CARBON		TOTAL NITROGEN	
	Unlimed	Limed	Unlimed	Limed
	per cent	*per cent*	*per cent*	*per cent*
Analyses made in 1909	1.22	1.22	0.1118	0.1118
Analyses at end of first 5-year period (1908–1912)	1.24	1.15	0.0969	0.0859
Analyses at end of second 5-year period (1913–1917)	1.19	1.07	0.1005	0.0879

The results of the nitrogen and carbon determinations seem to confirm a very widespread popular view which holds that lime tends to "burn out" the organic matter of the soil. In the popular mind, however, the "burning out" process is not well understood. It should be thought of as the result of biological processes in the main, rather than of chemical processes.

Moreover, it should be noted that in this case it was the carbonate of lime and not caustic or unslaked lime that was used. It would appear that the carbonate of lime made the conditions more favorable for the development of the organisms which break down organic matter, and thus more organic soil nitrogen was converted into the soluble form on the limed than on the unlimed series.

If the crops grown on this series had used all of this available nitrogen, then the yields should have been greater on the limed than on the unlimed plots. If the yields were not greater, then more nitrogen must have been lost from the limed than from the unlimed plots, since the former now contain less nitrogen than the latter. That this is so is shown by the averages reported in table 1, a summary of which is given in table 2.

* 32 pounds acid phosphate and 16 pounds muriate of potash.

The figures show a distinct loss of nitrogen from both the limed and unlimed sections during the period 1909–1912, but the loss from the limed section is 0.011 per cent more than from the unlimed section. Calculated to the acre basis, this is equivalent to more than 200 pounds of nitrogen for the plowed acre, or taking the first 5 years, an average loss over the unlimed plots of more than 40 pounds a year. There was also a distinct loss of carbon from the limed as compared with the unlimed plots during this period.

The second 5-year period shows a distinct loss in carbon from both series, but a greater loss from the limed than from the unlimed plots. For the nitrogen, on the other hand, a slight gain is shown for this period, but the difference of more than 200 pounds per acre in favor of the unlimed plots still remains.

That this difference in nitrogen content is not made up to the limed plots in a larger return of nitrogen through the crops from these plots is shown by the average yields of nitrogen and dry matter for the 10-year period, as shown in table 3.

TABLE 3

Average pounds of dry matter and nitrogen per acre in crops from limed and unlimed plots

	NITROGEN		DRY MATTER	
	Unlimed	Limed	Unlimed	Limed
	lbs.	*lbs.*	*lbs.*	*lbs.*
First 5-year period, 1908–1912*	40.66	40.76	3657	3669
Second 5-year period, 1913–1917†	28.31	31.07	2768	2926

* From Bul. 260, N. J. Agr. Exp. Sta.

† From unpublished results, N. J. Agr. Exp. Sta.

It will be noted that for the first 5-year period, the yields of nitrogen and dry matter are practically the same for the limed and unlimed sections. For the second 5-year period the limed plots show an increase of about 3 pounds of nitrogen and 160 pounds of dry matter per acre over the unlimed plots. However, against this slight increase, there must be set a loss of over 200 pounds of nitrogen per acre for the 10 years, or more than 20 pounds per acre annually. In what way, then, has the lime been a benefit either to the soil or to the crops during the 10-year period? Certainly in this case it has proved a detriment rather than a benefit. The yields on the limed plots have not been appreciably increased and at the end of the 10-year period the soil on these plots contains over 200 pounds per acre less of nitrogen than the soil on the unlimed plots. On the other hand, the acid condition of the unlimed soil acted as a partial preservative of the organic matter, while at the same time there was enough available nitrogen, including that which was applied, to produce a crop about equal to that produced on the limed plots. The limiting factor, whatever it was, affected the crop yields on the two sections about alike, but the reserve supply of nitrogen was being depleted more rapidly on the limed plots.

That the organic matter of the soil must be oxidized or "burned out" with the formation of nitrates and other simple compounds, is inevitable, and it is fortunate that it is so, for in this way available plant-food is formed out of unavailable crop residues and other organic matter, but it is just as inevitable that this loss must be made good in some way if yields are to be increased or even maintained, and the soil kept from wearing out, for the crop residues on light soils are not sufficient to maintain the reserve supply of organic matter.

It would not be safe to say that this will always happen on all types of soil, but it is safe to say that on ordinary well-drained loam soils the tendency will be in this direction if only non-legume crops are grown. It is very evident that on such soils, with modern tillage operations, the oxidation of organic matter is sufficiently rapid without the added stimulus of lime compounds.

There undoubtedly are acid peat soils, and poorly drained heavy clay soils, where there is a large amount of oxidizable organic matter or where oxidation proceeds very slowly, on which lime may be used in connection with the growing of non-legume crops to excellent advantage, but on loams or sandy loams, we may well question the advisability of using lime when non-legumes only are being grown. Under such a system the use of lime adds fuel to the fires of destruction.

The manner of the loss of this nitrogen is still an open question. Certainly a portion of it was lost in the drainage waters, and some escaped into the air as gaseous ammonia or nitrogen, but as to the relative amounts thus lost, we know little. Russell (6), after discussing the various ways by which nitrogen may be lost, says: "The exhaustion of the soil is, therefore, not due to the removal of the crop, but to the cultivation." He then refers to the enormous loss of nitrogen, nearly 70 per cent of the amount applied, from one of the Broadbalk wheat plots which receives 14 tons of stable manure annually. Because of the small amount of drainage water, he thinks the loss of nitrates on account of leaching is small. Russell says further:

> Experiments of this kind have led to the conclusion that some gaseous product is formed in addition to nitrates, and, as no sufficient amount of ammonia can be detected, it is supposed that gaseous nitrogen is given off. The conditions for this decomposition appear to be copious aeration, such as is produced by cultivation, and the presence of large quantities of decomposable organic matter. Now these are precisely the conditions of intense farming in old countries and of pioneer farming in new lands, and the result is that the reserves of soil and manurial nitrogen are everywhere being depleted at an appalling rate.

Russell refers to the fact that there are recuperative agencies at work, but adds that the gain in nitrogen does not go on indefinitely. The nitrogen content may be maintained at a high level when the ground is kept in grass and leguminous crops, and at a low level when it is continuously cultivated. "Unfortunately," he concludes, "on our present knowledge, it is impossible to maintain a high content of nitrogen on cultivated land except at a wasteful expenditure of nitrogenous manure."

Nearly forty years ago, Sir John Lawes (1) said very much the same thing but in different words, in speaking of experiments which he and Dr. Gilbert

were conducting on Broadbalk field. After discussing the question "what is exhaustion?" he sums up the matter thus:

> We have evidence of a very large loss in the accumulated stock of nitrogen based upon the assumption that my land was originally pasture; there is a further large loss during the period in which the land has been under experiment and growing unmanured corn crops. The crops are declining; the amount of nitrogen removed in the crops each year is declining; and, further, a considerable reduction of the nitrogen in the first 9 inches, with an indication of a small reduction in the second 9 inches, is shown by different analyses of the soil itself.

It may be added that the soil of Broadbalk field is well supplied with carbonate of lime, and this may have contributed to the rapid disappearance of the nitrogen, especially on those parts of the field where legumes were rarely grown.

SUMMARY

Lime in the carbonate form was used on a loam soil at the rate of 1 ton per acre for the first 5 years and 2 tons for the second 5 years in a 5-year rotation of corn, oats, wheat and 2 years of timothy. No legume crops were introduced. Twenty plots with different nitrogen treatment were thus limed and twenty similar plots with parallel nitrogen treatment were left without lime.

The total yields of dry matter and of nitrogen for the 10-year period were essentially the same for the two sections.

Analyses of the soil made soon after the work was started and again at the end of each 5-year period showed that there was a loss of nitrogen from both the limed and unlimed sections. However, the loss from the limed section was distinctly greater than from the unlimed section.

Thus at the end of the 10-year period, there was a positive loss rather than gain from the use of lime.

From this work it would appear that the practice of using lime on light to medium heavy soils, *when leguminous crops are not grown* in the rotation, may be questionable. Under such conditions it is quite possible that a slightly acid reaction may be desirable to prevent the too rapid oxidation of organic matter.

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THE LIME FACTOR IN PERMANENT SOIL IMPROVEMENT

II. Rotations with Legumes

J. G. LIPMAN and A. W. BLAIR

New Jersey Agricultural Experiment Station

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In the preceding paper, the authors have discussed the influence of lime on crops grown in a rotation which, so far as possible, excludes all legumes. In this paper, an attempt is made to show the influence of lime in four different rotation systems, all of which include some legume crops.

The soil on which this work was carried out is of the same character as and adjacent to that which was described in the preceding paper. It is a loam inclining to a sandy or gravelly phase and previous to 1908 when the work was started, had been badly neglected.

Twenty-eight $\frac{1}{20}$-acre plots were laid out and these divided into 4 sections of 7 plots each, each section being devoted to a different rotation but all sections having the same lime treatment. The rotations for the different sections are as follows:

	ROTATION 1 PLOTS 21–27	ROTATION 2 PLOTS 28–34	ROTATION 3 PLOTS 35–41	ROTATION 4 PLOTS 42–48
1913	Corn (rye, vetch, crimson clover)	Corn (rye, vetch, crimson clover)	Corn (rye, vetch, crimson clover)	Corn (rye, vetch, crimson clover)
1914	Oats (soybeans and cowpeas)	Potatoes	Potatoes (rye)	Oats and peas, millet
1915	Wheat	Rye	Tomatoes (rye, vetch, crimson clover)	Rye and vetch, rape
1916	Timothy and clover	Timothy and clover	Lima beans (rye, vetch, crimson clover)	Rye, cowpeas (rye)
1917	Timothy and clover	Timothy and clover	Cucumbers (rye and vetch)	Oats and peas, cowpeas

The first plot in each section is the check plot, that is, it receives no lime treatment. The second, third and fourth plots in each section received in 1913, $\frac{1}{2}$, 1 and 2 tons, respectively, of finely ground calcium limestone per acre, and the fifth, sixth and seventh plots received $\frac{1}{2}$, 1 and 2 tons, respectively, of magnesian limestone per acre. This lime treatment was intended to last throughout the 5-year rotation, 1913 to 1917.

Samples of soil were not collected when the work was begun but samples which were taken from three of the plots in 1909 showed an average nitrogen content of a little over 0.10 per cent. In 1913 and again in 1918, samples were collected from all plots for lime-requirement and total nitrogen and carbon determinations. The results of the determinations on the two sets of samples are shown in another place in this paper.

It should be explained here that the results of this work for the first five years, 1908 to 1912, have been published (1, 2), and will not be included in this paper except in so far as they may be needed to make clear the work of the second 5-year period.

In summarizing this work, it was stated that with comparatively few exceptions, both forms of lime increased the yield of dry matter and nitrogen

TABLE 1

Average increase in yield of nitrogen, in pounds per acre, over the check plots, for the non-magnesian and magnesian limestone sections, 1908–1912

		1908	1909	1910	1911	1912
		lbs.	*lbs.*	*lbs.*	*lbs.*	*lbs.*
Plots 21–27 (Rotation 1)	Non-magnesian limestone	7.95	1.97	5.95	2.00	2.67
	Magnesian limestone	14.91	9.70	11.23	10.47	11.70
Plots 28–34 (Rotation 2)	Non-magnesian limestone	10.27	0.00	9.74	2.79	8.55
	Magnesian limestone	3.33	0.00	17.17	4.06	5.97
Plots 35–41 (Rotation 3)	Non-magnesian limestone	5.57	3.93	*	8.51	
	Magnesian limestone	7.21	5.93	*	6.77	*
Plots 42–48 (Rotation 4)	Non-magnesian limestone	7.71	2.75	52.65	16.74	27.89
	Magnesian limestone	6.41	12.73	70 00	0.00	20.05

* Nitrogen determinations not made.

over the yields given by the check plots. It was also pointed out that in the majority of cases, the dry matter of crops from the limed plots showed a higher percentage of nitrogen than dry matter from the unlimed plots.

The influence of the lime is clearly brought out by the figures given in table 1 which show the average increase, in pounds of nitrogen per acre, over the check plots, for the two limestone treatments. With only slight exception, a fair gain is shown for all rotations. The most pronounced exception is the potato crop on plots 28 to 34 in 1909.

It is significant that the largest gains are shown for the forage crops rotation, plots 42 to 48. In 1910, on these plots there was a gain of 52.65 pounds of nitrogen per acre for the non-magnesian limestone and 70 pounds per acre for the magnesian limestone. In some cases, the gain is greater for the one form of lime and in other cases for the other form.

The average percentage of nitrogen in the soil samples collected in 1913 is somewhat less than the average of the three samples taken in 1909. This, it is pointed out, appears to indicate a gradual loss of nitrogen even though the plots had received a moderate application of nitrogenous fertilizers and had had the benefit of two or more leguminous crops during the rotation. The land, however, was producing good crops which were with one exception being taken off the land, and thus more nitrogen was being removed in the crops than was being applied in the form of commercial fertilizers.

The second 5-year period embraces the years of 1913 to 1917 and the results are reported for the two forms of lime as yield of dry matter, per cent of nitrogen in the dry matter, and total nitrogen removed in the crop. This plan is carried out for the four rotations and it is thus possible to note the influence of the lime on the yield of dry matter and nitrogen and also to compare the two forms of lime as used in the different quantities.

ROTATION 1—GENERAL FARM CROPS

Plots 21–27—1913 to 1917

This rotation consisted of one year of corn, one of oats, one of wheat and two of timothy and clover. Since this was the beginning of the second 5-year period, there was a timothy and clover sod to be plowed under for corn. Notes made May 1, 1919, state that on the check plot (plot 21, no lime) there was a poor stand of clover in scattered weak bunches and that on the limed plots the stand was fair to good.

The land was fitted for corn and finely ground limestone applied in accordance with the plans already outlined. Fertilizers also were applied on the acre basis as follows:

Acid phosphate, 300 pounds
Muriate of potash, 100 pounds
A mixture of fish and tankage equivalent to 200 pounds of fish

This, it will be noted furnished nitrogen equivalent to about 100 pounds of nitrate of soda.

Reed's Yellow Dent corn was planted on June 2 and this received the usual cultivation during the season. In late September, the corn was harvested, weighed and samples dried and prepared for analysis.

A cover crop of rye, vetch and crimson clover was seeded in the corn at the last cultivation. Notes made in the early spring of 1914 state that the rye on the no-lime plot was about 4 inches high but that there was no vetch or crimson clover on this plot. The rye was thicker on the other plots and there was also more vetch and crimson clover.

On April 14 this cover crop was plowed under and about one week later fertilizers were applied and the plots seeded to oats. The fertilizers were the same as those used for the corn the previous year, except that dried fish was used at the rate of 200 pounds per acre.

In July it was noted that the oats on plot 21 (check) were more mature but the crop was not so heavy as on the lime-treated plots.

On July 27 the oats were harvested and samples prepared for analysis. Following the oats the land was disked and seeded to a mixture of soybeans and cowpeas as a cover crop. The beans and peas grew finely and on September 14 were plowed under preparatory to seeding the wheat. The plants were 6 to 7 inches high and appeared to be well inoculated. Fertilizers were applied as follows:

	lbs. per acre.
Acid phosphate	300
Muriate of potash	100
High-grade tankage	200

On September 30, wheat was seeded at the rate of 7½ pecks per acre. Notes made April 15, 1915, and again on May 1 state that the wheat on plot 21 was not so good as on the other plots. The wheat was harvested July 9, weighed, and samples prepared for analysis. The land was then fitted for timothy and clover and fertilizers applied on the acre basis as follows:

	lbs.
Acid phosphate	400
Muriate of potash	100
Nitrate of soda	50

The full application of nitrate was 200 pounds per acre, but 150 pounds of this was reserved for a top-dressing to be applied in the spring. The timothy and clover were seeded on September 2 and this seeding resulted in a good stand. On April 13, 1916, the remainder of the nitrate of soda was applied as a top-dressing. A note made June 1 states that there was practically no clover on plot 21. The crop was harvested July 5, weighed and sampled. On August 22, a second cutting of this crop was made, and it was noted at this time that the timothy was too short to be a factor and that there were only a few bunches of clover on plot 21. The plots that received 2000 pounds of limestone were about three-quarters covered with clover, while those that received 4000 pounds were entirely covered. The crop was weighed and samples prepared for analysis.

On November 9, acid phosphate and muriate of potash were applied to the timothy and clover at the rate of 300 pounds and 100 pounds per acre, respectively.

The following spring nitrate of soda was applied as a top-dressing at the rate of 200 pounds per acre.

On June 1 it was noted that there was not very much clover on any of the plots. This is shown by the low nitrogen content of the hay, analysis of which is reported in table 3. The crop was harvested July 5, weighed and sampled for analysis. As already indicated, samples of all these crops were carefully dried and the yield of dry matter calculated on an acre basis. Nitrogen determinations were made on all samples, thus providing for the calculation of the total nitrogen in the crops.

The yields of dry matter and total nitrogen per acre and the percentage of nitrogen in the dry matter for the various crops for the 5-year period are shown in tables 2, 3 and 4.

Considering first the yields of dry matter as shown in table 2, it will be noted that with only slight exception, the plots receiving the lime treatment have given better yields than the check plots. The most notable exception is the oats crop of 1914, where the check plot yielded more grain than any of the treated plots. In the case of the other crops the check plot invariably yielded less than the treated plots.

TABLE 2

Rotation 1—Yield of dry matter, in pounds per acre, for 5 years, 1913–1917

PLOT	LIMESTONE APPLIED PER ACRE	1913		1914		1915		1916		1917	TOTAL		ANNUAL INCREASE OVER CHECK	
		Corn		Oats		Wheat		Timothy and clover	Red clover	Timothy and clover				
		Grain	Stover	Grain	Straw	Grain	Straw				Grain	Stover straw hay	Grain	Stover straw hay
	lbs.	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*
21	Check	850	2650	660	860	1040	1240	3600	200	2620	2550	11,170		
	Calcium-limestone section													
22	1000	1225	2800	480	800	1200	1440	3680	980	3520	2905	13,220	118.3	410
23	2000	1400	2950	600	1040	1260	1640	4380	1420	3640	3260	15,070	236.7	780
24	4000	1675	3150	600	1020	1240	1480	4400	1660	3500	3515	15,210	321.7	808
	Average	1433	2967	560	953	1233	1520	4153	1353	3553	3227	14,500	225.6	666
	Magnesian-limestone section													
25	1000	1850	3500	620	1040	1240	1600	4440	1100	3520	3210	15,200	220.0	806
26	2000	1875	3500	600	1120	1260	1680	4620	1920	3800	3735	16,640	395.0	1094
27	4000	2000	3200	640	1040	1220	1600	4540	1800	4220	3860	16,400	436.7	1046
	Average	1742	3400	620	1067	1240	1627	4533	1607	3847	3602	16,080	350.6	982

With very slight exception, there is some increase in yield with each increase in the amount of calcium limestone applied, and likewise an increase from the 1000 to the 2000-pound application of magnesian limestone. On the other hand, there is not so often an increase in yield from the 2000 to the 4000-pound application in this section. It is to be noted, however, that the average yields on the magnesian-limestone section are without exception, larger than the corresponding yields for the calcium-limestone section.

The average *annual* increase for the check plots for the calcium-limestone section is for the grain 225.6 pounds, and for the straw, hay, etc., 666 pounds, whereas the corresponding figures for the magnesian-limestone section are

TABLE 3

Rotation 1—Yield of nitrogen, in pounds per acre, removed by crops for the years 1913–1917

PLOT	LIMESTONE APPLIED PER ACRE	1913		1914		1915		1916		1917	TOTAL NITROGEN GRAIN, HAY, ETC.	ANNUAL INCREASE OF NITROGEN OVER CHECK
		Corn		Oats		Wheat		Timothy and clover	Red clover	Timothy and clover		
		Grain	Stover	Grain	Straw	Grain	Straw					
	lbs.	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*
21	Check	10.31	15.30	13.36	6.29	20.47	3.66	31.18	4.32	19.91	124.80	
	Calcium-limestone section											
22	1000	15.35	17.76	10.48	6.56	24.30	3.96	41.29	25.03	28.51	173.24	9.69
23	2000	18.37	21.90	13.27	8.90	25.16	6.30	52.74	35.87	30.90	213.41	17.72
24	4000	24.12	25.21	13.16	7.64	24.63	4.07	52.58	44.97	29.72	226.10	20.26
Average		19.28	21.62	12.30	7.70	24.70	4.78	48.87	35.29	29.71	204.25	15.89
	Magnesian-limestone section											
25	1000	17.17	23.99	13.60	7.88	25.13	5.34	45.78	28.90	27.81	195.60	14.16
26	2000	25.71	26.57	13.10	10.28	24.80	4.79	54.79	51.30	32.26	243.60	23.76
27	4000	29.78	24.40	15.12	8.90	24.24	5.50	52.16	47.61	34.56	242.27	23.49
Average		24.22	24.99	13.94	9.02	24.72	5.21	50.91	42.60	31.54	227.16	20.47

TABLE 4

Rotation 1—Per cent of nitrogen in dry matter of crops for the years 1913–1917

PLOT	LIMESTONE APPLIED PER ACRE	1913		1914		1915		1916		1917
		Corn		Oats		Wheat		Timothy and clover	Red clover	Timothy and clover
		Grain	Stover	Grain	Straw	Grain	Straw			
	lbs.	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
21	Check	1.213	0.573	2.024	0.731	1.968	0.295	0.866	2.161	0.760
	Calcium-limestone section									
22	1000	1.253	0.652	2.184	0.820	2.025	0.275	1.122	2.554	0.810
23	2000	1.312	0.761	2.211	0.856	1.997	0.384	1.204	2.526	0.849
24	4000	1.440	0.820	2.193	0.749	1.987	0.275	1.195	2.709	0.849
Average		1.335	0.744	2.196	0.808	2.003	0.311	1.174	2.596	0.836
	Magnesian-limestone section									
25	1000	1.272	0.711	2.193	0.758	2.027	0.334	1.031	2.627	0.790
26	2000	1.371	0.790	2.184	0.918	1.968	0.285	1.186	2.672	0.849
27	4000	1.489	0.810	2.362	0.856	1.987	0.344	1.149	2.645	0.819
Average		1.377	0.770	2.246	0.844	1.994	0.321	1.122	2.648	0.819

for the grain 350.6 pounds, and straw, hay, etc., 982 pounds. Attention should be called to the very wide difference between the yield of red clover on the check plot and the treated plots for 1916. This crop, as is well known, is especially susceptible to the unfavorable soil condition brought about by the deficiency of lime.

What has been said with reference to the yield of dry matter will apply in most cases to the yield of total nitrogen shown in table 3. With very few exceptions, the lime treatments have resulted in an increase of total nitrogen over the check plot. The 2000-pound application of both forms of lime, in nearly all cases, shows an increase over the 1000-pound application. In a number of cases, on the other hand, the 4000-pound application shows no increase over the 2000-pound application. The total yields of nitrogen for the 5 years are as follows:

	LIMESTONE APPLIED	YIELD
	lbs. per acre	*lbs. per acre*
Check		124.8
Calcium limestone	1000	173.2
	2000	213.4
	4000	226.1
Magnesian limestone	1000	195.6
	2000	243.5
	4000	242.3

From these figures it will be noted that with the calcium limestone 4000 pounds gave a slightly higher yield than 2000 pounds. With the magnesian limestone, the yields with the 2000 and 4000-pound applications are practically the same.

The annual increase for the calcium limestone plots over the check plots ranges from 9.69 pounds, with the 1000-pound application to 20.26 pounds with the 4000-pound application. In the case of the magnesian limestone the increase is 14.16 pounds with the 1000-pound application, 23.76 pounds with the 2000-pound application, and 23.49 pounds with the 4000-pound application. Excluding the 1000-pound applications, the increases per acre will average above 20 pounds per year. Thus the increase for one year would more than pay the cost of the limestone.

The percentage of nitrogen in the dry matter as reported in table 4 is of especial interest. With very few exceptions, it is higher in the samples from the limed plots than in those from the check plots. This is true of the grain and also of the straw, corn stover and hay. In earlier publications we have called attention to this effect of lime and have suggested, in the case of the legume crops, that the lime tends to establish soil conditions favorable to the development of those organisms which aid the plant in storing up atmos-

pheric nitrogen. The higher percentage of nitrogen in non-leguminous plants is no doubt in part an indirect effect of the stimulation of the symbiotic organisms, that is, the utilization of nitrogen which was secured through leguminous plants, and in part the result of the stimulation of those organisms which nitrify organic matter in general.

To increase the crop yield means much, but to increase also the nitrogen content of the crop adds still further to its total value.

The average percentages of nitrogen in the crops from the two sections differ but slightly, that is, the average percentage of nitrogen in the crops from the magnesian-limestone section is not appreciably greater than the average in crops from the calcium-limestone section.

Referring again to the total yield of nitrogen (table 3) it may be pointed out that with 2000 pounds per acre of magnesian limestone, the timothy and clover crop of 1916 removed slightly more than 100 pounds of nitrogen per acre. In comparison with this, it will be noted that the corn crop of 1913—grain and stover—removed about one-half as much nitrogen. The smallest amount of nitrogen was removed by the oat crop of 1914. This was somewhat below the normal, because the oats shattered badly at the time of harvesting.

The fertilizers which were applied during the 5 years carried a total of about 108 pounds of nitrogen. The crops on the calcium-limestone section removed an average during the same period of a little more than 200 pounds per acre, and those on the magnesian-limestone section removed an average of nearly 230 pounds per acre. There is good reason for believing that this excess over the amount applied is being drawn from the atmosphere largely through the legume crops. If it is not being thus secured then the soil is gradually being depleted of its nitrogen supply. This question will be further discussed in connection with the table showing the percentage of nitrogen in the soil.

ROTATION 2—GENERAL FARM CROPS WITH POTATOES

Plots 28–34—1913 to 1917

This rotation consists of one year of corn, one of potatoes, one of wheat and two of timothy and clover. As in the case of rotation 1, plots 21 to 27, the timothy and clover sod preceded the corn and the corn crop was fertilized and cared for in the same way as in rotation 1. Early in August a cover crop of rye, vetch and crimson clover was seeded in the corn. Notes taken April 8, 1914, show that the rye was thin on plots 28 and 29, and also that there was not much vetch and crimson clover on these plots. This cover crop was plowed under about the middle of April, 1914, and fertilizers applied on the acre basis as follows:

	lbs.
Acid phosphate	300
Muriate of potash	100
Dried fish	200

Early in May the plots were planted to Green Mountain potatoes. After these had been planted, it was decided that the first application of fertilizers was not sufficient and the following additional application was made per acre—100 pounds of acid phosphate and 200 pounds of muriate of potash, thus making the total application 400 pounds of acid phosphate, 300 pounds of muriate of potash and 200 pounds of dried ground fish. This fertilizer was spread broadcast.

The crop was cultivated and sprayed in the usual way throughout the season. Potatoes were dug about the twenty-fifth of August and later the plots were disked preparatory to seeding to rye. Fertilizers were applied on the acre basis as follows:

	lbs.
Acid phosphate	300
Muriate of potash	100
High-grade tankage	200

The plots were seeded to rye at the rate of 6 pecks per acre (vetch and crimson clover were not included in this seeding).

Notes taken April 15, 1915, state that the rye was 8 to 10 inches high at that time. The rye was harvested as grain the last of June and about the last of August the land was prepared and seeded to timothy and clover. For this crop fertilizers were applied on the acre basis as follows:

	lbs.
Acid phosphate	400
Muriate of potash	100
Nitrate of soda	50

On April 13, 1916, these plots received a further top-dressing of nitrate of soda equivalent to 150 pounds per acre. On June 6, the timothy on these plots was about 22 to 24 inches high. There was very little clover on the check plot (no. 28), though there was a fine stand on the other plots. On July 5 the crop was harvested and weighed and the samples prepared.

On August 1 the second growth of clover on these plots was reported as about 12 to 15 inches high, but it was noted that there was very little on plot 28. This second growth was cut and weighed and samples prepared August 23. On November 9 the plots were fertilized at the following rate per acre:

	lbs.
Acid phosphate	300
Muriate of potash	100

On April 12, 1917, nitrate of soda was applied at the rate of 200 pounds per acre, no nitrate having been applied the previous fall. The effect of this top-dressing was soon apparent, and the timothy made a good growth. The clover was poor. The crop was harvested and weighed July 5 and samples prepared for analysis. The yield of dry matter and total nitrogen from these plots and the percentage of nitrogen in the dry matter are reported in tables 5, 6 and 7.

The yields of dry matter for the 5-year period are summarized in table 5. For the corn and the timothy and clover the lime treatment shows fair increases over the check plots. For the potatoes and rye—1914 and 1915—the yields on the treated plots are slightly less than those on the check, with the exception of the potatoes on the calcium limestone section. The failure of these crops to respond to the lime treatment was probably due to the partial failure of the cover crop which preceded the potatoes, and the absence of any legume cover crop preceding the rye. Or to express the matter an-

TABLE 5

Rotation 2—Yield of dry matter, in pounds per acre, for the 5-year period, 1913–1917*

PLOT	LIMESTONE APPLIED PER ACRE	1913		1914	1915		1916		1917	TOTAL†		YEARLY INCREASE OVER CHECK	
		Corn			Rye								
		Grain	Stover	Potatoes	Grain	Straw	Timothy and clover	Red clover	Timothy and clover	Grain	Forage, hay, etc.	Grain	Stover, hay
	lbs.	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*
28	Check	1050	2425	6200	1400	2680	3920	660	3500	2450	13,185		
	Calcium-limestone section												
29	1000	1850	2575	7040	1360	2600	4320	960	3680	3210	14,135	380	238
30	2000	1900	2425	7100	1400	2700	4820	1160	4440	3300	15,545	425	590
31	4000	2025	2725	6560	1280	2560	4520	1580	4500	3305	15,885	428	675
Average....		1925	2575	6900	1347	2620	4553	1233	4207	3272	15,188	411	501
	Magnesian-limestone section												
32	1000	2000	2700	5960	1440	2600	4620	1080	3960	3440	14,960	495	444
33	2000	2050	2700	5620	1520	2800	4440	1760	3840	3570	15,540	560	589
34	4000	2200	2525	5240	1320	2560	4200	1660	3580	3520	14,525	535	335
Average....		2083	2642	5607	1427	2653	4420	1500	3793	3510	15,008	530	456

* Field weight of potatoes.

† Potatoes not included in total.

other way, the lime could not exert its full benefit in the partial or complete absence of those crops through which it manifests itself most readily. The most notable increases occur with the mixed timothy and clover and clover alone. The latter shows an increase of more than 100 per cent with the magnesian limestone and almost as much with the calcium limestone.

The yields of total nitrogen which are shown in table 6 follow quite closely the yields of dry matter. In the case of the corn (grain) and the red clover the increase amounts to over 100 per cent. The potatoes and rye on the check plot yielded very nearly the same amount of nitrogen as on the treated plots.

On the calcium-limestone plots, there was recovered an average of nearly 228 pounds of nitrogen per acre for the 5-year period and on the magnesian-limestone plots an average of about 234 pounds for the same period, or more than 45 pounds per acre per annum. During the 5 years, there was applied to these plots about 108 pounds of nitrogen, or 22 pounds per year. Apparently we have here a loss of about 24 pounds per acre annually, but undoubtedly this loss was more than made up by the nitrogen secured through the legume crops.

Table 7 shows the percentage of nitrogen in the dry matter of the different crops. It will be noted that, with very few exceptions, the crops from the lime-treated plots—both sections—show a higher percentage of nitrogen than the crops from the check plots. This is in accord with the results secured in rotation 1.

ROTATION 3—CORN, POTATOES AND MARKET GARDEN CROPS

Plots 35–41—1913 to 1917

The corn in this rotation was preceded by the timothy and clover sod and received the same treatment as that in rotations 1 and 2, and the potatoes the same treatment as those in rotation 2. Following the potatoes, the plots were disked, fertilizers applied and rye seeded at the rate of 6 pecks per acre. The fertilizer treatment was the same as that given to plots 28 to 34 at this time.

On April 15, 1915, the rye on these plots was about 8 to 10 inches high. On May 3, the plots were disked preparatory to plowing under the rye as a green manure. The plots were plowed on June 2 and fertilizers applied for the tomatoes on the acre basis as follows:

	lbs.
Acid phosphate	600
Muriate of potash	300
Nitrate of soda	200
Dried blood	160

Chalk's Early Jewel tomatoes were set out and later in the season received the usual cultivation and other attention. Picking began about the middle of August and continued until the middle of September, five pickings being made.

Unfortunately, samples were not saved from each plot but a composite sample was made. Thus it is necessary in calculating the nitrogen removed by the tomatoes to base the calculations on the analysis of this composite sample.

Following the tomatoes, the land was disked and seeded to a mixture of rye, vetch and crimson clover. The amount of rye in the mixture was small and consequently a thin stand was secured. Notes made on April 1, 1916,

TABLE 6

Rotation 2—Yield of nitrogen, in pounds per acre, removed by crops for the years 1913–1917

PLOT	LIMESTONE APPLIED PER ACRE	1913		1914	1915		1916		1917	TOTAL NITROGEN	YEARLY INCREASE OVER CHECK
		Corn		Potatoes	Rye		Timothy and clover	Red clover	Timothy and clover		
		Grain	Stover		Grain	Straw					
	lbs.	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs,*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*
28	Check	14.29	19.00	22.47	19.96	8.23	38.96	14.93	27.30	165.14	
	Calcium-limestone section										
29	1000	28.29	22.31	23.84	19.53	7.20	38.62	23.03	29.44	192.26	5.42
30	2000	32.98	28.17	20.90	21.21	8.29	56.25	26.45	39.03	233.28	13.63
31	4000	35.37	35.06	20.34	20.15	8.60	62.24	39.63	36.00	257.39	18.45
Average		32.21	28.51	21.69	20.30	8.03	52.37	29.70	34.82	227.64	12.50
	Magnesian-limestone section										
32	1000	31.36	25.16	21.72	21.40	7.98	52.67	26.49	34.41	221.19	11.21
33	2000	31.92	30.20	21.14	21.98	8.60	46.18	44.62	37.52	242.16	15.40
34	4000	34.06	26.79	19.26	19.87	8.60	55.15	41.48	34.65	239.86	14.94
Average		32.45	27.38	20.71	21.08	8.39	51.33	37.53	35.53	234.40	13.85

TABLE 7

Rotation 2—Per cent of nitrogen in dry matter of crops for the 5-year period, 1913–1917

PLOT	LIMESTONE APPLIED PER ACRE	1913		1914	1915		1916		1917
		Corn		Potatoes	Rye		Timothy and clover	Red clover	Timothy and clover
		Grain	Stover		Grain	Straw			
	lbs.	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
28	Check	1.361	0.751	1.783	1.426	0.307	0.994	2.262	0.780
	Calcium-limestone section								
29	1000	1.529	0.830	1.703	1.436	0.277	0.894	2.399	0.800
30	2000	1.736	1.097	1.560	1.515	0.307	1.167	2.280	0.879
31	4000	1.746	1.235	1.614	1.574	0.336	1.377	2.508	0.800
Average. ...		1.670	1.054	1.626	1.508	0.307	1.146	2.396	0.826
	Magnesian-limestone section								
32	1000	1.568	0.889	1.872	1.486	0.307	1.140	2.453	0.869
33	2000	1.557	1.067	1.854	1.446	0.307	1.040	2.535	0.977
34	4000	1.548	0.998	2.006	1.505	0.336	1.313	2.499	0.968
Average		1.558	0.985	1.911	1.479	0.317	1.164	2.496	0.938

state that the cover crop on these plots was fair. Later notes show that the vetch and crimson clover were poor on plot 35 and very good on plot 41.

On May 8 this cover crop was plowed under and on the nineteenth fertilizers were applied on the acre basis as follows:

	lbs.
Acid phosphate	600
Muriate of potash	300
Nitrate of soda	100

About one week later, Burpee's bush lima beans were planted. Notes made July 1 show that the beans were somewhat irregular in growth. On August 1 they were in bloom. On the tenth of August the cover crop consisting of rye, vetch and crimson clover was seeded in the beans. Between September 11 and October 20, four pickings of beans were made. Notes made April 12, 1917, show that there was a good cover crop on these plots. On May 15 the cover crop was plowed under and fertilizers applied on the acre basis as follows:

	lbs.
Acid phosphate	400
Muriate of potash	100
Nitrate of soda	160
Tankage	200

On the twenty-fifth of May the plots were planted to White Spine cucumbers. These received the usual cultivation and other attention during the summer. A number of pickings were made between July 27 and August 31. Samples were taken from each plot for nitrogen determinations.

After the cucumbers were off the plots were disked and seeded to rye and vetch.

The yields of total dry matter (or marketable vegetables), the total nitrogen and percentage of nitrogen in the dry matter (or marketable vegetables) are shown in tables 8, 9 and 10.

From the figures given in table 8 it will be noted that the limestone-treated plots, in nearly all cases, show a distinct increase over the check plots. This is true for both forms of limestone and if we may judge from the averages, one form does not have much advantage over the other. The cucumbers on the limed plots show notable increases over the check plots. The yield of potatoes on the calcium-limestone section is greater than the yield on the magnesian-limestone section. This is true also of the potatoes grown in rotation 2. It is doubtful, however, if the differences are sufficient to have any particular significance.

It should be noted that the yields of potatoes, tomatoes and cucumbers are the yields at the time of harvesting and not the yields of dry matter.

Table 9 shows the total yield of nitrogen for the various crops. With only one exception (lima beans on plot 41) the lime-treated plots show pronounced increases over the check plots.

TABLE 8

Rotation 3—Yield of dry matter (or harvesting weights), in pounds per acre, for the years 1913–1917

PLOT	LIMESTONE APPLIED PER ACRE	1913		1914	1915	1916		1917	TOTAL		
		Corn		Potatoes	Ripe tomatoes	Lima beans		Marketable cucumbers	Grain	Stover	Potatoes tomatoes cucumbers
		Grain	Stover			Seeds	Pods				
	lbs.	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*
35	Check	1475	2650	4800	24,080	480	260	8,138	1955	2910	37,018
	Calcium-limestone section										
36	1000	1675	2850	6320	28,550	660	332	11,618	2335	3182	46,488
37	2000	1750	3125	6300	27,860	860	448	13,536	2610	3573	47,696
38	4000	2025	3325	5740	25,610	720	360	11,688	2745	3685	43,038
Average.....		1817	3100	6120	27,340	747	380	12,281	2563	3480	45,741
	Magnesian-limestone section										
39	1000	1775	2975	5680	25,454	540	300	13,432	2315	3275	44,566
40	2000	2100	3275	6260	27,720	660	288	13,482	2760	3563	47,462
41	4000	2200	3200	5100	28,924	360	200	13,496	2560	3400	47,520
Average.....		2025	3150	5680	27,366	520	263	13,470	2545	3413	46,516

NOTE: Potatoes, tomatoes and cucumbers weighed as harvested.

TABLE 9

Rotation 3—Yield of nitrogen, in pounds per acre, removed by crops for the years 1913–1917

PLOT	LIMESTONE APPLIED PER ACRE	1913		1914	1915	1916		1914	TOTAL NITROGEN	YEARLY INCREASE OVER CHECK
		Corn		Potatoes	Ripe tomatoes	Lima beans		Marketable cucumbers		
		Grain	Stover			Seeds	Pods			
	lbs.	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*
35	Check	22.11	20.87	15.42	40.55	14.52	2.17	9.50	125.14	
	Calcium-limestone section									
36	1000	25.61	23.50	16.20	48.08	19.97	2.46	14.82	150.64	5.1
37	2000	27.27	26.12	19.14	46.92	26.33	3.03	18.34	167.15	8.4
38	4000	30.76	24.62	20.74	43.13	20.51	2.30	14.96	157.02	6.4
Average....		27.88	24.75	18.69	46.04	22.27	2.60	16.04	158.27	6.6
	Magnesian-limestone section									
39	1000	24.51	22.01	16.41	42.86	16.74	2.56	16.94	142.03	3.4
40	2000	30.87	25.41	19.25	46.68	20.76	2.40	16.94	162.31	7.4
41	4000	34.06	27.99	16.34	48.71	11.43	2.88	15.86	157.27	6.4
Average....		29.81	25.14	17.33	46.08	16.31	2.61	16.58	153.87	5.7

The averages for the two sections run very close together, though the average of the potatoes for the calcium-limestone section has a slight advantage over the corresponding average for the magnesian-limestone section.

Attention should be called to the fact that the total amount of nitrogen recovered in the crop is less, by more than fifty pounds, than the total amounts recovered from the two preceding rotations. This calls attention to the fact that market garden crops, although generally giving larger and more profitable yields than general farm crops, take from the land less nitrogen than the latter.

TABLE 10

Rotation 3—Per cent of nitrogen in dry matter of crops for the 5-year period, 1913–1917

PLOT	LIMESTONE APPLIED PER ACRE	1913		1914	1915	1916		1917
		Corn		Potatoes*	Ripe tomatoes	Lima beans		Marketable cucumbers†
		Grain	Stover			Seeds	Pods	
	lbs.	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
35	Check	1.499	0.820	1.676	0.1684‡	3.025	0.835	0.121
	Calcium-limestone section							
36	1000	1.529	0.860	1.373	0.1684	3.025	0.742	0.133
37	2000	1.558	0.879	1.569	0.1684	3.062	0.677	0.141
38	4000	1.519	0.769	1.819	0.1684	2.849	0.640	0.130
Average		1.535	0.836	1.587	0.1684	2.979	0.686	0.135
	Magnesian-limestone section							
39	1000	1.381	0.771	1.578	0.1684	3.100	0.854	0.135
40	2000	1.470	0.810	1.631	0.1684	3.146	0.835	0.128
41	4000	1.548	0.939	1.738	0.1684	3.174	1.438	0.124
Average		1.466	0.840	1.649	0.1684	3.140	1.042	0.129

* Potatoes dried.

† Tomatoes and cucumbers sampled as harvested.

‡ Composite sample.

The total amount of nitrogen applied to these crops during the 5 years was about 150 pounds, or 30 pounds per acre, while the average amount removed on the lime-treated sections was about 155 pounds, or a yearly average of about 31 pounds per acre.

Table 10 shows the percentage of nitrogen in the different crops. The increase in percentage due to the lime treatment is not so consistent as in rotations 1 and 2, but there are as many plots for which the percentage of nitrogen is above that of the check as there are plots with the percentage below the check. The nitrogen determinations were made on the potatoes after they had been thoroughly dried but, as already explained, they were made on the tomatoes and cucumbers as harvested.

ROTATION 4—FORAGE CROPS

Plots 42–48—1913 to 1917

The corn which was planted on these plots in 1913 had been preceded in 1912 by oats and peas followed by cowpeas, both of which crops were taken off. As no winter cover crop was seeded, the plots remained bare during the winter of 1912 and 1913. This corn received the same attention and treatment as the corn in the other rotations. On August 6 a cover crop of rye, vetch and crimson clover was seeded in the corn. On April 21, 1914, this cover crop was plowed under, and notes made at that time state that there was a fair crop of vetch and crimson clover on all plots except plot 42 which had none. On April 23, fertilizers were applied to the oats and peas at the following rate:

	lbs. per acre
Acid phosphate	300
Muriate of potash	100
Fish	200

On April 24 oats and peas were seeded at the rate of 3 bushels per acre. On July 6 these were cut as a forage crop and the land immediately prepared for seeding to barnyard millet. The millet was seeded July 8. Notes made under date of August 4 state that there was a thin stand and that weeds were coming in to the detriment of the millet. The millet was cut August 28, the weights recorded and samples prepared for analysis. On August 31, the plots were plowed and prepared for winter vetch. Fertilizers were applied at the following rate per acre:

	lbs.
Acid phosphate	300
Muriate of potash	100

Notes made April 15, 1915, state that there was a very poor stand of vetch on plot 42. The vetch was good on the other plots. The poor stand on plot 42 was no doubt the result of winter-killing due to adverse soil conditions. On June 1, it was estimated that there was only one-fourth of a stand on this plot. On the other plots, the vetch was 20 to 26 inches high. The vetch was cut June 9 and the ground plowed and seeded to Dwarf Essex rape. Fertilizers were applied on the acre basis as follows:

	lbs.
Acid phosphate	300
Muriate of potash	100
Nitrate of soda	200

The rape was harvested September 15 but was not an entirely satisfactory crop on account of a rather heavy growth of crab-grass. The land was again plowed and seeded to rye, fertilizers being applied on the acre basis as follows:

	lbs.
Acid phosphate	400
Muriate of potash	100
Nitrate of soda	50

On November 1 a good stand of rye was noted on all the plots.

On April 13, 1916, a top-dressing of nitrate of soda was made at the rate of 150 pounds per acre. The rye made a good growth and on June 1 was cut as a forage crop. The land was plowed, fertilized and seeded to Whippoorwill cowpeas. The fertilizer treatment consisted of acid phosphate at the rate of 400 pounds and muriate of potash at the rate of 200 pounds per acre. Notes made August 1 state that there was a thin stand of the cowpeas and that there was much crab-grass among them. On September 19 the cowpeas were cut for hay. The record shows that the crop was about 50 per cent crab-grass. On September 28 the plots were disked and seeded to rye at the rate of 4 pounds per plot. A good stand was secured. On April 17, 1917, the rye was plowed under and fertilizers applied at the following rate per acre:

	lbs.
Acid phosphate	300
Muriate of potash	100
Dried fish	200

Oats and peas were seeded at the rate of 3 bushels per acre. On July 1 the oats and peas were about 8 to 10 inches high but the check plot was noted as being the poorest. They were cut as hay July 12 and the ground disked and seeded to Whippoorwill cowpeas at the rate of 6 pounds per plot. Notes of August 1 state that there was a good stand. The check plot, however, was the poorest. On October 2 they were harvested as hay. The plots were prepared with a spring-tooth harrow on October 12 and rye was seeded at the rate of 4 pounds per plot. The yields for these plots during the 5-year period, together with the total yield of nitrogen and percentage of nitrogen in the crop are shown in tables 11, 12 and 13.

The yield of dry matter for the 5-year period is shown in table 11. Again, with slight exception, the lime-treated plots show a distinct increase over the check plots. In the calcium-limestone section, the oats and peas grown in 1914 show an average increase of 760 pounds per acre and the vetch grown the next year shows a much larger average increase. It may be explained here that the vetch on the check plot was almost an entire failure.

In most cases the averages for the magnesian-limestone section run quite close to those for the calcium-limestone section. However, for the millet the yield on the former is less than on the latter. For the vetch of 1915 the yield is almost twice as much from the magnesian-limestone section as from the calcium-limestone section. The average yearly increase in grain for the calcium-limestone section amounts to 533 pounds and for the magnesian-limestone section to 258 pounds. The corresponding figures for the corn stalks and hay are 1021 and 1073 pounds. This is equivalent to $4\frac{3}{5}$ to $9\frac{1}{2}$ bushels of grain and $\frac{1}{2}$ ton of stalks and hay per acre, which represents the annual gain over the no-lime plot.

The yield of nitrogen for this rotation is shown in table 12. In nearly all cases the lime treatment has resulted in a substantial increase in yield of nitrogen over the check plot. The most pronounced exception is the millet in the magnesian-limestone section in 1914. It should be recalled that this crop came near being choked out by crab-grass, and this accounts in part for the low yields. Attention may be called to the high yield of nitrogen from the vetch crop of 1915. For the calcium-limestone section, there is an average of 48 pounds per acre, and for the magnesian-limestone section an average of nearly 79 pounds per acre.

TABLE 11

Rotation 4—Yield of dry matter, in pounds per acre, for the 5-year period 1913–1917

PLOT	LIMESTONE APPLIED PER ACRE	1913		1914		1915		1916		1917		TOTAL		YEARLY INCREASE OVER CHECK	
		Corn													
		Grain	Stover	Oats and peas	Millet	Vetch	Rape	Rye	Cowpeas	Oats and peas	Cowpeas	Grain	Forage, hay, etc.	Grain	Stover and hay
	lbs.	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*
42	Check	1350	2675	1520	400	220	1700	2240	1940	2120	1160	1350	13,975		
	Calcium-limestone section														
43	1000	1775	2825	2200	480	840	1840	2660	2240	2600	1240	1775	16,925	425	590
44	2000	1825	3000	2200	620	1400	2120	2780	2540	2820	1600	1825	19,080	475	1021
45	4000	2050	3275	2440	520	2160	2120	3120	2880	2680	2040	2050	21,235	700	1452
Average		1883	3033	2280	540	1467	2027	2853	2553	2700	1627	1883	19,080	533	1021
	Magnesian-limestone section														
46	1000	1550	2425	2120	140	2180	1660	2880	2360	3040	1440	1550	18,245	200	854
47	2000	1625	2900	2080	280	2920	2040	2960	2780	2940	1480	1625	20,380	275	1281
48	4000	1650	2550	1920	300	2960	2460	2400	2380	2660	1760	1650	19,390	300	1083
Average		1608	2625	2040	240	2687	2053	2747	2507	2880	1560	1608	19,338	258	1073

The highest yield—nearly 90 pounds—was on the magnesian-limestone plot which received 4000 pounds per acre. Next to the vetch, the oats and peas and the cowpeas gave the largest yields of nitrogen. In 1917, the total nitrogen secured for these two crops on the magnesian-limestone section amounts to more than 100 pounds for each limestone treatment.

The total nitrogen for the 5 years averages $373\frac{2}{3}$ pounds for the calcium-limestone section and $381\frac{1}{2}$ pounds for the magnesian-limestone section, or more than 75 pounds per year. There was applied to these plots a total of about 108 pounds of nitrogen per acre for the 5 years, or nearly 22 pounds per year.

TABLE 12

Rotation 4—Pounds of nitrogen per acre removed by crops for the 5-year period 1913–1917

PLOT	LIMESTONE APPLIED PER ACRE	1913		1914		1915		1916		1917		TOTAL NITROGEN IN GRAIN, HAY, ETC.	YEARLY INCREASE IN NITROGEN OVER CHECK
		Corn		Oats and peas	Millet	Vetch	Rape	Rye	Cow-peas	Oats and peas	Cow-peas		
		Grain	Stover										
	lbs.	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs.*	*lbs*
42	Check	18.37	18.58	25.20	4.74	7.08	16.68	23.50	28.52	27.41	32.31	202.39	
	Calcium-limestone section												
43	1000	25.03	20.29	41.18	6.33	28.67	18.42	29.47	28.34	42.61	34.77	275.11	14.5
44	2000	26.65	25.46	41.58	8.79	49.62	22.09	28.36	41.12	49.01	46.72	339.40	27.4
45	4000	28.52	26.91	46.80	7.28	65.82	24.38	36.07	59.73	56.09	64.87	416.47	42.8
Average.....		26.73	24.22	43.18	7.47	48.04	21.63	31.30	43.06	49.24	48.79	373.69	28.23
	Magnesian-limestone section												
46	1000	21.56	18.19	37.91	2.22	60.08	19.24	30.79	54.89	57.64	47.19	349.71	29.5
47	2000	22.44	20.58	35.65	3.79	86.52	23.26	30.49	65.44	54.57	50.35	393.09	38.1
48	4000	24.26	20.52	38.78	4.07	89.63	27.08	23.09	54.91	64.08	55.30	401.72	39.9
Average.....		22.75	19.76	37.45	3.36	78.74	23.19	28.12	58.41	58.76	50.95	381.51	35.83

TABLE 13

Rotation 4—Per cent of nitrogen in dry matter of crops for the years 1913–1917

PLOT	LIMESTONE APPLIED PER ACRE	1913		1914		1915		1916		1917	
		Corn		Oats and peas	Millet	Vetch	Rape	Rye	Cow-peas	Oats and peas	Cow-peas
		Grain	Stover								
	lbs.	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
42	Check	1.361	0.721	1.658	1.186	3.216	0.981	1.049	1.470	1.293	2.785
	Calcium-limestone section										
43	1000	1.410	0.751	1.872	1.319	3.413	1.001	1.108	1.265	1.639	2.804
44	2000	1.460	0.899	1.890	1.417	3.544	1.042	1.020	1.619	1.738	2.920
45	4000	1.391	0.860	1.918	1.400	3.047	1.150	1.156	2.074	2.093	3.180
Average		1.420	0.837	1.893	1.379	3.335	1.064	1.095	1.653	1.823	2.968
	Magnesian-limestone section										
46	1000	1.391	0.790	1.788	1.587	2.756	1.159	1.069	2.326	1.896	3.277
47	2000	1.381	0.731	1.714	1.355	2.963	1.140	1.030	2.354	1.856	3.402
48	4000	1.470	0.860	2.020	1.355	3.028	1.101	0.962	2.307	2.409	3.142
Average		1.414	0.794	1.841	1.432	2.916	1.133	1.020	2.329	2.054	3.274

Thus there was removed in the crop more than three times as much as was applied in the fertilizers. The average annual increase over the check plot for the calcium-limestone section is 28 pounds per acre and for the magnesian-limestone section 35 pounds per acre. These increases are equal to, and in some cases exceed, the total yields in some of the wheat and rye crops reported in rotation 1.

The percentage of nitrogen in the dry matter is shown in table 13. In the majority of cases there is a higher percentage in samples from the lime-treated plots than in those from the check plots. This is well brought out by comparing the percentage as shown for the check plots with the corresponding averages for the two lime-treated sections. With only two exceptions the latter show a higher percentage of nitrogen in the dry matter than does the check plot. The high percentage of nitrogen in the vetch of 1915 and the cowpeas grown in 1917 is noteworthy, the highest analysis with vetch being 3.54 per cent and the highest with cowpeas 3.40 per cent. The oats and peas show an average close to 2 per cent, while the non-legume crops such as corn, rape and rye show an average of a little over 1 per cent for the rye and rape and 1.4 per cent for the corn and millet.

These figures present a strong argument for growing leguminous crops wherever they can be brought into the rotation to good advantage.

THE INFLUENCE OF THE LIME TREATMENT ON THE NITROGEN CONTENT AND LIME REQUIREMENT OF THE SOIL

Lime requirement

In connection with the foregoing discussion, the figures presented in table 14 are of interest. At the end of each 5-year period, nitrogen and lime-requirement determinations were made on samples of soil from the rotation plots. For these determinations composite samples were taken by making a number of borings to a depth of $6\frac{2}{3}$ inches. The samples were thoroughly mixed and after being dried were passed through a 2-mm. sieve to remove coarse material.

In most cases the soils show a gradual decrease in lime requirement as the amount of limestone was increased. At the end of the first 5-year period, the average lime requirement for the check plots was close to 1200 pounds per acre, while for the plots that received the 2 tons of limestone per acre it was less than 500 pounds. In 1917, at the end of the second 5-year period, the average for the check plots was about 1300 pounds per acre, whereas those plots that received 2 tons of limestone per acre were either alkaline or had a low lime requirement. From this it would appear that the 2-ton application was quite sufficient for a period of 5 years; indeed, where only 1 ton was used the soil had a low lime requirement at the end of the 5 years.

There does not appear to be very much difference in neutralizing power between the calcium limestone and the magnesian limestone.

TABLE 14

Lime requirement and percentage of nitrogen of soils from plots that have received different quantities of lime, 1908–1917

PLOT	LIMESTONE TREATMENT	LIME (CaO) REQUIREMENT PER 2,000,000 POUNDS OF SOIL		NITROGEN	
		1912*	1917†	1912	1917
	Rotation 1—General farm crops				
		lbs.	*lbs.*	*per cent*	*per cent*
21	Nothing	1200	1200	0.077	0.0794
22	0.5 ton $CaCO_3$ per acre	1000	600	0.075	0.0798
23	1.0 ton $CaCO_3$ per acre	600	400	0.075	0.0791
24	2.0 ton $CaCO_3$ per acre	000	alk.	0.081	0.0901
25	0.5 ton $CaCO_3MgCO_3$ per acre	600	400	0.091	0.0959
26	1.0 ton $CaCO_3MgCO_3$ per acre	700	400	0.093	0.1015
27	2.0 ton $CaCO_3MgCO_3$ per acre	000	alk.	0.092	0.1010
	Rotation 2—General farm crops and potatoes				
28	Nothing	800	1400	0.094	0.0994
29	0.5 ton $CaCO_3$ per acre	800	1000	0.097	0.1019
30	1.0 ton $CaCO_3$ per acre	600	400	0.094	0.0931
31	2.0 ton $CaCO_3$ per acre	100	alk.	0.098	0.1041
32	0.5 ton $CaCO_3MgCO_3$ per acre	700	400	0.093	0.1025
33	1.0 ton $CaCO_3MgCO_3$ per acre	400	alk.	0.091	0.0954
34	2.0 ton $CaCO_3MgCO_3$ per acre	300	200	0.089	0.0966
	Rotation 3—Corn, potatoes, market garden crops				
35	Nothing	1100	1200	0.093	0.0921
36	0.5 ton $CaCO_3$ per acre	800	1000	0.094	0.0912
37	1.0 ton $CaCO_3$ per acre	600	800	0.081	0.0837
38	2.0 ton $CaCO_3$ per acre	400	alk.	0.075	0.0808
39	0.5 ton $CaCO_3MgCO_3$ per acre	1100	1000	0.077	0.0800
40	1.0 ton $CaCO_3MgCO_3$ per acre	700	400	0.080	0.0837
41	2.0 ton $CaCO_3MgCO_3$ per acre	500	400	0.082	0.0800
	Rotation 4—Forage crops				
42	Nothing	1200	1400	0.084	0.0899
43	0.5 ton $CaCO_3$ per acre	1100	1200	0.095	0.0998
44	1.0 ton $CaCO_3$ per acre	700	800	0.099	0.1012
45	2.0 ton $CaCO_3$ per acre	600	400	0.089	0.0864
46	0.5 ton $CaCO_3MgCO_3$ per acre	1100	1200	0.079	0.0773
47	1.0 ton $CaCO_3MgCO_3$ per acre	500	400	0.067	0.0679
48	2.0 ton $CaCO_3MgCO_3$ per acre	300	alk.	0.098	0.0652

* Limestone applied in 1908.

† Limestone applied in 1913.

Percentage of nitrogen in soils

Nitrogen was determined by the Kjeldahl method and in most cases the results reported are an average of four or more carefully made determinations.

It will be recalled that in Part I of this paper, it was pointed out that with the 5-year rotation of non-legumes the limed section was poorer in nitrogen than the unlimed section at the end of both the first and the second 5-year periods. Furthermore, it was shown that the crops on the limed section were only slightly larger than those on the unlimed section. In other words, the lime actually resulted in a considerable dissipation or loss of nitrogen over and above any loss shown by the unlimed plots.

From the figures shown in table 14, it is evident that the lime treatment has not generally resulted in a depletion of the soil nitrogen as compared with the check, or no-lime plot. This may be more clearly shown by comparing the percentage of nitrogen in samples of soil from the check plot for each rotation, with the average percentage of nitrogen in samples from the six lime-treated plots for that rotation.

The figures are as follows:

		1912	1917
		per cent	*per cent*
Rotation 1	Check (no. 21)	0.077	0.079
	Average, no. 22 to 27	0.084	0.091
Rotation 2	Check (no. 28)	0.094	0.099
	Average, no. 29 to 34	0.094	0.099
Rotation 3	Check (no. 35)	0.093	0.092
	Average, no. 36 to 41	0.082	0.083
Rotation 4	Check	0.084	0.090
	Average, no. 43 to 48	0.088	0.083

It will be noted that for rotation 1 the lime-treated plots, on an average, show a higher nitrogen content than the check plots; for rotation 2 the average percentage for the limed plots is the same as for the check plot. For rotation 3, the average for the lime-treated plot is about 0.01 per cent less than the percentage for the check plot. For rotation 4 the difference is slightly in favor of the lime-treated plots in 1912 and the check plot in 1917. It will be noted that the figures for 1917 run very close to those for 1912 in both cases.

The lime-treated plots show the greatest gain during the 5 years in rotation 1, and the most loss in rotation 4.

Certainly in this case it can not be said that the lime treatment has been a failure. It has, with only few exceptions, resulted in increased yields, which in several instances have been large, and in addition the nitrogen content of

the soil has been fairly well maintained. In the meantime fair crops have been taken from the land. The oats crops, it must be admitted, have been small, partly because of loss from shattering in the field. The potato crops were not fully successful, because the land is not well adapted to potatoes. With these exceptions, and taking the crops for the 10-year period, the yields have probably been above the average for the locality.

It should be pointed out that these results have been secured without the use of farm manure and with only a very moderate amount of commercial nitrogenous fertilizer. Minerals have been applied in generous amounts in order that a deficiency of these might not become a limiting factor.

From the data presented, it is evident that the limestone which was applied has been an important factor in increasing the yields on the rotation plots described here, but it should be remembered that this effect has been more indirect than direct. Its presence in the soil has favored those organisms which associate themselves with the leguminous plants and has thus enabled those plants to get from the air a larger supply of nitrogen than was obtained by plants grown where the conditions are unfavorable for the nitrogen-fixing organisms.

SUMMARY

Four 5-year rotations were carried out on a loam soil. In each rotation there were seven plots; one unlimed and one each that received 1000, 2000 and 4000 pounds per acre of calcium limestone, and one each that received like amounts of magnesian limestone.

In each rotation legume crops were introduced either as one of the main crops or as a green-manure crop between the main crops.

Two 5-year periods for each rotation have been completed.

Acid phosphate and muriate of potash were used in liberal amounts. Light applications of commercial nitrogenous fertilizers were made. No farm manure was used.

During the 10 years the limed plots, with only slight exception, have yielded distinctly larger crops and more total nitrogen than the unlimed plots.

In most cases, the yields were larger with the 2000 and 4000-pound applications than with the 1000-pound application. The two forms of limestone gave results which are quite similar. There appears to be a slight difference in favor of the magnesian limestone.

In the majority of cases, the percentage of nitrogen was higher in crops from the limed than from the unlimed plots.

The use of lime thus resulted in a gain in both quantity of the crop produced and also in the quality.

Analyses of the soil show, in a number of cases, a higher nitrogen content for limed than for unlimed plots; in other cases, the two are about on a level as to nitrogen content and in a few cases, there has apparently been a depletion of the nitrogen in the limed plots.

This work, taken in connection with the work presented in the preceding paper, would seem to indicate that in using lime emphasis should be laid on its power to make conditions favorable for the organisms associated with leguminous crops rather than on its power simply to neutralize soil acids. In other words, its value is more indirect than direct.

ACKNOWLEDGMENT

The authors wish to give due credit to Dr. H. C. McLean for a large part of the analytical work reported in the two papers.

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COLORIMETRIC DETERMINATION OF HYDROGEN-ION CONCENTRATION WITHOUT BUFFER MIXTURES, WITH ESPECIAL REFERENCE TO SOILS

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Although it was appreciated at least as early as 1903 (9) that colorimetric measurements of hydrogen-ion concentration might be based upon the properties of the indicators themselves, without involving the use of solutions of known hydrogen-ion concentration—the so-called "buffer mixtures"—no body of data has yet been secured which can be relied upon to furnish a good, if only approximate, system. At present the various indicators are used in connection with buffer mixtures, though the work of Barnett and Chapman (2) makes the use of buffer mixtures unnecessary for much of the range covered by the indicator phenolsulfonphthalein. These investigators use the indicator in a procedure almost identical with that to be recommended in this paper, after having standardized their technique without reference to dissociation curve or constant.

There are available sufficient data from which tables might be calculated for a system for the approximate determination of hydrogen-ion concentration by means of certain of the modern indicators and without the use of buffer mixtures; but evidence has not hitherto been published showing whether such calculations would be justified. This would depend upon whether or not the behavior of these indicators conforms sufficiently well to the equation one would wish to apply, and whether the technical procedures, which it is convenient to use, are free from objection.

The writer has tested these points, determining the apparent dissociation constant and the form of the apparent dissociation curve by simple methods, such as are serviceable in routine, for enough of the indicators selected by Clark and Lubs (4, 6) to cover the range between the hydrogen-ion exponents 3.2 and 9.7. It was the intention to carry out the study to a higher degree of precision, as some of the indicators would repay this, but recent conditions put a stop to the work; and the results, being already of sufficient precision for the ordinary purposes of the writer, are put forward for the convenience of others. A method is presented, the necessary data for which are contained in a single table (table 7). The method should be of especial use in orienting experiments, or in occasional experiments involving hydrogen-ion exponent

measurements, either where it is unnecessary to push to the highest degree of precision obtainable, or where the investigator may be content to carry out his measurements to his limit of precision and to record his results in such a form that they may be more closely interpreted when a more precise study of the indicators shall have been completed.[1]

All results have been expressed in terms of Sörensen's hydrogen-ion exponent, instead of the hydrogen-ion concentration itself. The exponent is merely the common logarithm of the reciprocal of the concentration, when the concentration is given in gram-ions per liter in the usual way. As a reaction becomes more alkaline (or less acid) the hydrogen-ion concentration decreases, but the exponent increases, passing through the value 7.0 (at about 20–25°) at physico-chemical neutrality.

PRINCIPLE OF THE METHOD

The theory underlying the colorimetric determination of the hydrogen-ion exponent without buffer mixtures is in short the following. At any given hydrogen-ion exponent the condition of a dissolved indicator is fixed, a certain definite percentage being in the acid form and the rest being in the alkaline form. We may assume that light is absorbed independently by the two forms of the indicator, and hence that the absorption, and in consequence of this the residual color emerging, will be the same whether the two forms are present together in the same solution or whether the forms are separated for convenience in two different vessels and the light passes through one vessel after the other. Therefore, if we know what these percentages are for a given indicator in a given buffer mixture, we can imitate the color shown in the buffer mixture by dividing the indicator in the proper proportion between two vessels, and putting part of it into the acid form with excess of acid, and the rest into the alkaline form with excess of alkali.

For an indicator which acts like a monobasic acid, the percentages in the alkaline and in the acid form should be related to the hydrogen-ion exponent which produces the percentage relation in accordance with the equation

$$\mathrm{pH} = k + \log \frac{(\text{alkaline form})}{(\text{acid form})}$$

where pH is the hydrogen-ion exponent of a given solution, k is the apparent dissociation constant of the indicator expressed as a hydrogen-ion exponent, and the ratio (of which the common logarithm is taken) is the ratio existing

[1] For this purpose the room temperature and the particular indicator used should be stated. Variations of temperature are usually disregarded, and buffer mixtures calibrated at 18° or 20° are used at higher temperatures without any statement as to what the temperature is. In using the method presented here the errors involved in disregarding temperatures may not be the same as if buffer mixtures are used.

between the concentrations of the alkaline and the acid forms.[2] The ratio is equivalent to what will later be called the "drop-ratio," and another form of the equation is therefore

$$\text{pH} = k + \log \text{ "drop-ratio."}$$

If 5 drops of indicator solution are placed in a test-tube in dilute alkali and 5 drops placed in another test-tube in dilute acid, and compared with various buffer mixtures containing 10 drops of indicator solution until the color seen on looking through one buffer mixture is the same as that seen on looking through the two 5-drop tubes, the volume of all the tubes having been made the same, the drop-ratio is equal to 1; and since the log of 1 is 0, the hydrogen-ion exponent of the buffer mixture is equal to k, the apparent dissociation constant of the indicator expressed as an exponent. This is the principle used by Salm (16) in determining the affinity constants in some indicators.

How well the theoretical equation applies in the case of any particular indicator must be determined by experiment. It is to be noted that if the indicator is a monacid base it will act like a monobasic acid, as far as the equation is concerned. Also, the indicator, though known to be dibasic, may nevertheless act within a limited range of hydrogen-ion exponent as a monobasic acid; namely, if the two dissociation constants (representing the two stages of dissociation) are far enough apart on the exponent scale. This appears to be the case with the sulfonphthaleins (6, 12). In the case of phenolphthalein (which is not a sulfonphthalein) the equation cannot apply, as is well known from the work of Acree (1) and others. If the data given by Rosenstein (17) are used to plot a curve with pH and the percentage transformation into alkaline form as the variables, the curve is found to be a straight line as far as the measurements extend. The percentage of transformation increases faster with the increase of the exponent than the theoretical equation given above demands.

[2] The equation may easily be derived (by taking the logarithms of both sides and changing signs) from the following one, which is the general equation corresponding to a particular one given by Stieglitz (19), his equation 7', page 1122:

$$H^{\times} = k \frac{\text{(acid form)}}{\text{(alkaline form)}}$$

where the parentheses indicate concentrations. Stieglitz showed that the equation in this form takes account of any tautomeric changes concerned in the change of color, and it is easy to see from his discussion that the form of the equation is the same whether the indicator is a weak acid or a weak base, provided that it behaves within the range of color change under consideration as a monobasic acid or a monacid base. The constant k includes the affinity constant of the tautomeric change as well as the dissociation constant of the acid or base, and if the indicator is a base it includes also the dissociation constant of water. The constant k has therefore been called the apparent [Noyes (16)] or total (Acree) dissociation constant.

Tizard (20) studied the color change of methyl red, using a colorimeter in yellow light, and thus measuring only the change of intensity of the red color. The yellow alkaline color is not apparent under such illumination. He found the indicator to be dibasic, and the two dissociation constants to be near enough together to cause some interference. It does not follow, however, that the theoretical equation given above may not be found to hold, and, conversely, a verification of the equation does not prove the indicator to be strictly "monobasic." As a matter of fact, as will be shown later, the data of Tizard can be used to verify the equation. At higher acidities than those included in the useful range, the color was found to diminish, and it would appear necessary, in more precise work than that contemplated by the use of the method here presented, to regulate with care the strength of the acid solution used to develop the full acid color of this indicator. No difficulty was actually experienced in the present work, and some experiments, made with the use of 0.05*M* buffer mixtures, failed to discover a significant diminution at the same points found by Tizard.

CALCULATIONS BASED ON THE THEORETICAL EQUATION

By means of the technique to be described, the per cent transformation into the alkaline form may be determined in steps of 10 per cent. Table 1 is useful in applying the equation.

Once the equation is shown to be valid for a particular indicator, a table may be made out for the indicator similar to table 7 (to be given later) by adding to each log value the value of the dissociation constant expressed as an exponent, paying attention to the fact that the first five log values are negative numbers (and are not therefore technically logarithms). The resulting figures give then the exponents corresponding to the various drop-ratios. The intervals of the system are about 0.2 pH. If a less precise system is desired for special purposes a 5-drop system may be used instead of the 10-drop system described below, and the desired table may be prepared by simple omission of unnecessary values. Such a system would provide intervals of 0.4 pH and would require indicator solutions of double the strength specified in table 7.

EXPERIMENTS ON WHICH THE METHOD IS BASED

In the study of each indicator a comparator was used which differed from that shown in figure 1 in having only four holes for test-tubes instead of six. Uniform tubes 1.5 cm. in external diameter and 15 cm. long were used. A pair of tubes was prepared containing together 10 drops of indicator solution, the 10 drops being distributed in the two tubes in one of the drop-ratios, 1 : 9, 2 : 8, 3 : 7, and so on, the contents of one tube of the pair being made alkaline and the contents of the other, acid. Each pair of tubes was placed in turn in one side of the comparator and in the other side were placed a tube of water

(in the back) and a tube containing 10 drops of the indicator solution in one of the buffer mixtures studied by Clark and Lubs (5). The tubes were nearly uniform, and the volume was made the same in all the tubes, usually 5 to 6 cc.,

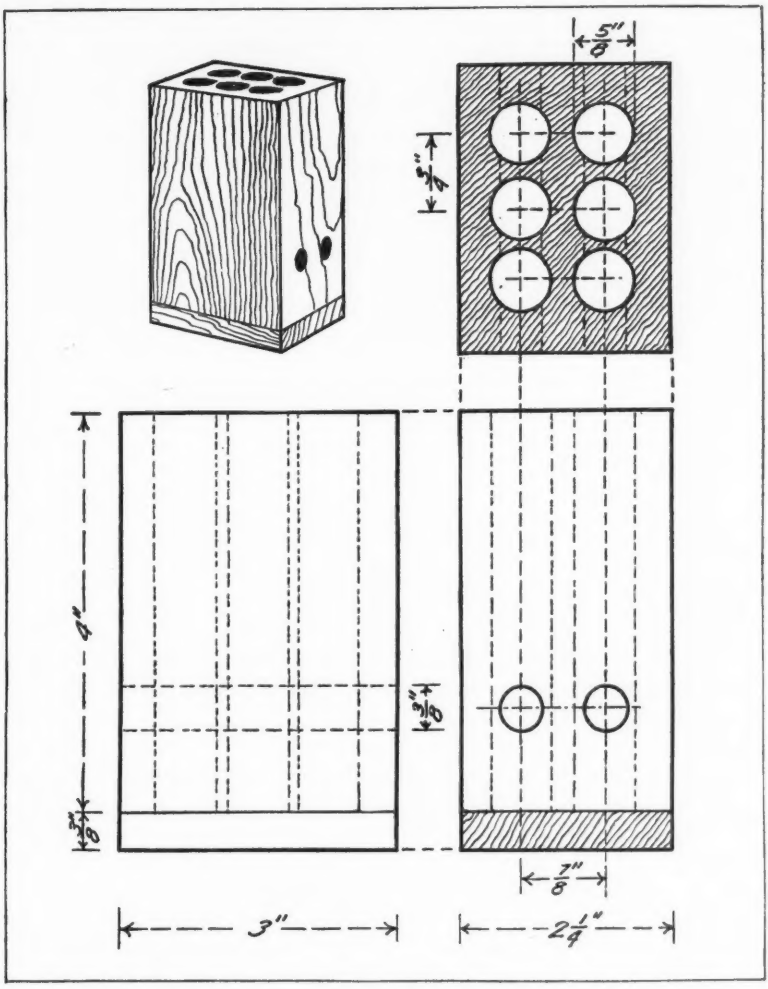

FIG. 1. COMPARATOR FOR HYDROGEN-ION EXPONENT MEASUREMENTS

distilled water being added for this purpose to the tubes of the pair. Various buffer tubes were tried until a match was obtained. If the color seen through the pair of tubes fell in an interval between two buffer tubes a quick estimate was made of the fraction of the interval, and this fraction was recorded.

After the measurements were finished the results were calculated from the determined hydrogen-ion exponent values of the buffer solutions. In this way the pairs of tubes of the various ratios were treated as if each pair had been a single solution of unknown hydrogen-ion concentration, and its hydrogen-ion exponent measured colorimetrically. The result may then be termed the hydrogen-ion exponent value of the pair.

A few pairs of tubes were also studied containing a total of 5 drops in the same volume of solution, and others containing a total of 20 drops. In this way the indicators were studied at all concentrations which could be used with test-tubes of about the given dimensions in the given procedure. It was not to be expected that the dissociation constant could show perceptible change with changes of 100 per cent in concentration, since the indicator was in very dilute solution in any case, from 0.00001 to 0.00002 molecular. When alcoholic solutions were used an effect was sometimes seen when the larger quantities of indicator solution were added. This was probably due to change in the nature of the solvent, the concentration of alcohol increasing to about 4 to 6 per cent when 20 drops were used.

TABLE 1

Logarithm values for the various drop-ratios

	DROP-RATIO										
	1:9	1.5:8.5	2:8	3:7	4:6	5:5	6:4	7:3	8:2	8.5:1.5	9:1
Log value.....	−0.95	−0.75	−0.60	−0.37	−0.18	0	0.18	0.37	0.60	0.75	0.95
Approximate log value.....	−0.95	−0.75	−0.6	−0.4	−0.2	0	0.2	0.4	0.6	0.75	0.95

There were at hand a series of buffer mixtures somewhat old. In order to reduce the effect of the personal equation these solutions, which were no longer exact, were used in preference to fresh ones, and the hydrogen-ion exponent of each in turn was determined at practically the same time and at nearly the same room temperature at which they were used. The hydrogen-ion measurements were made in the Clark electrode vessel (3) with mechanical shaking in a well insulated box. The automatic temperature regulation was not used; and the temperature of the box was about that of the room but was far more constant, varying hardly a degree per day. As reference electrode a saturated potassium chloride, calomel, electrode was used and the hydrogen-ion exponents were calculated from the figures given by Michaelis (15). This electrode had been in use for about three years and had been frequently checked with satisfactory results against Clark and Lubs' 0.05*M* acid potassium phthalate solution (5) and Michaelis' standard acetate solution (15). At about 25°, Clark and Lubs' value for 20°, 3.97, was closely checked; at 30° the value found by the above method of reference was about 4.01. In the case of the standard acetate the results were always about 0.4

to 0.5 millivolt (0.01 pH) higher than those given by Michaelis; this being due possibly to the fact that the Clark electrode vessel gives a more certain equilibrium after 5 minutes' shaking than Michaelis seems to have attained with his hydrogen electrode in a considerably longer time. He states that 30 minutes or longer may be required in the case of standard acetate solution, which would seem from his account to take a longer time to reach equilibrium in his apparatus than many other solutions.

In the use of the Clark electrode vessel the vessel was first flooded with electrolytic hydrogen (after filling with water or the solution, unless the air was known to be displaced by previous determinations), and then washed with the fluid; then the fluid admitted, and the vessel rocked for 5 minutes. Hydrogen was not bubbled through the liquid, this procedure not being necessary except in very precise work; and in fact being suitable only for solutions containing no volatile acids or bases (unless the hydrogen is suitably washed before entering the electrode vessel.) It was noted that, because of the volatility of acetic acid, successive determinations of the standard acetate mixture did not check unless the portion of the fluid remaining in the test-tube portion of the vessel was discarded. Such portions evidently lost acetic acid during the 5 minutes' shaking. A small sheet platinum electrode was used, which was coated freshly every day with palladium black and subsequently treated in the usual manner, as described elsewhere (10).

The results of the measurements of the hydrogen-ion exponent value of the various pairs of tubes having drop-ratios 1 : 9, 2 : 8, etc., are given in tables 2 and 3. For the calibration of a system for measurement of hydrogen-ion exponent it is better not to use these individual figures, as they contain experimental errors, but to smooth out the errors by means of the theoretical equation, provided the data are well represented by it. To examine this the values of the constants were calculated by means of the equation and are summarized in table 4. In tables 2, 3 and 4, parentheses are used to enclose figures affected by unusual uncertainties of measurement. In some cases there is an evident effect on the constant of the use of 20 drops of alcoholic indicator solution. Aside from these cases, the apparent dissociation constant is really constant within the experimental error of the color comparisons. This error varies of course with the different indicators, being relatively great with bromphenol blue and bromcresol purple, and small with the red indicators, especially phenol red. The question is of course left open whether or not any inexactness of the equation might be established if means were taken to secure more precise color estimations. It is clear that the equation is entirely suitable for smoothing out the accidental errors.

The results will now be taken up further with each indicator in turn, including some results not summarized in the tables.

Bromphenol blue (Tetrabromo-phenolsulfonphthalein; M. W.,[3] 670). This indicator, because of its dichromatism, sometimes gives trouble with turbid

[3] Molecular weight.

solutions, as was discussed by Clark and Lubs, who recommended (6) a screened light (yellow) for use when difficulty is experienced in daylight. All the figures reported in tables 2 and 3 were obtained by daylight measurements, but this indicator, as well as some of the others, was also studied in the yellow screened light. The constants obtained were not quite the same, being 4.00 for the aqueous indicator solution, and 3.99 for the alcoholic indicator solution (10-drop series), as against 4.06 and 4.04 for the daylight measurements.

TABLE 2

Hydrogen-ion exponent values found for the various pairs. Indicators used in water solution

DROP-RATIO	INDICATOR					
	Brom-phenol blue	Methyl red	Brom-cresol purple	Phenol red	Cresol red	Thymol blue (alkaline range
1:9	3.20	4.20	5.36	6.83	6.94	(8.01)
2:8	3.38	4.35	5.61	7.09	7.44	8.27
3:7	3.69	4.65	5.79	7.34	7.67	8.51
4:6	3.83	4.83	6.10	7.52	7.92	8.63
5:5	4.02	4.96	6.21	7.74	8.08	8.76
6:4	4.21	5.12	6.40	7.92	8.30	9.02
7:3	4.30	5.32	6.72	8.11	8.43	9.10
8:2	4.73	5.56	6.89	8.32	8.67	9.42
9:1		(5.85)	7.09	(8.59)	8.84	(9.57)
1:4		4.38				
2:3		4.77		7.56		
3:2	4.35			7.85		
4:1	(4.8)			8.34	8.71	
2:18	3.15		5.31	6.82	7.06	7.87
4:16	3.40		5.56	7.09	(7.41)	8.23
6:14			5.82	7.29	7.67	8.47
8:12			5.96			8.69
10:10				7.72		8.79
12:8						8.97
14:6				(8.00)	8.45	9.16
16:4		5.50				9.37
18:2		5.96				9.70
Room temperature	31°	30°	30°	29°	24°	24°
k	4.06	4.96	6.26	7.72	8.08	8.82
Indicator solution used (per cent)	0.008	0.003	0.012	0.004	0.008	0.008

The discrepancies, which of course cannot be due to a real change of the dissociation constant, are in all cases within the possible error of interpolation, and are no doubt entirely due to this error, as in certain cases the comparison was repeated with the error of interpolation halved by the use of buffer mixtures only 0.1 pH apart, and the discrepancy was in those cases reduced correspondingly. The discrepancy was apparently due to the use of the screened light in a room not otherwise darkened, and also to certain relative

positions of the screened light and the windows. If measurements are to be made with the screened light in a room which cannot well be darkened, the screened light should be so placed that white light does not enter the eye from one side or the other. Because of these considerations, the values found for daylight have been used in the preparation of tables for use either in daylight or in the yellow light. Similar discrepancies due to the same cause were noted with some of the other indicators.

TABLE 3

Hydrogen-ion exponent values found for the various pairs. Indicators used in alcoholic solution

DROP-RATIO	INDICATOR				
	Brom-phenol blue	Methyl red	Brom-cresol purple	Brom-thymol blue	Brom-hymol blue
1:9	3.38	4.00	(5.23)	6.10	(6.10)
2:8	3.40	4.42	5.60	6.38	(6.35)
3:7	3.67	4.69	5.82	6.68	6.66
4:6	3.78	4.85	5.82	6.86	6.85
5:5	4.04	5.01	6.12	7.04	7.06
6:4	4.21	5.19	6.29	7.23	7.29
7:3	4.44	5.34	6.48	7.47	7.47
8:2	(4.74)	5.56	6.67	7.79	7.70
9:1		5.82	(7.13)	7.98	
1:4		4.44			
2:3					
3:2			6.44		
4:1			(7.13)		
2:18	3.10		5.14		6.12
4:16	3.37		5.42		
6:14		4.64	5.66		6.72
8:12			5.85		
10:10	3.90		6.10		7.02
12:8			6.27		
14:6	4.28	5.34	6.44		
16:4	4.44		6.76		7.57
18:2	4.89	5.88	(7.02)		7.87
Room temperature	29°	27°	30°	25°	27°
Indicator solution per cent	0.008	0.008	0.024	0.03	0.015
Alcohol (per cent) in indicator solution	95	60	95	60	60

A few measurements were made toward determining the temperature coefficients, using for this purpose fresh phthalate buffer mixtures, spaced at 0.1 pH intervals. They were made up and checked at 20°. Measurements of the temperature coefficients of the buffers were not made. The aqueous indicator solution was used and the pair having the drop-ratio 7 : 3 was studied. The buffer mixtures were kept in a water bath regulated at a given temperature and were removed an instant at a time to permit quick

measurement in the comparator of the hydrogen-ion exponent value of the 7:3 pair. No certain difference in the value could be seen on varying the temperature in several steps from 15 to 50°. The values could be estimated only within 0.1 pH. This result does not mean that the temperature coefficient is necessarily negligible, since the change of hydrogen-ion exponent of the buffers might possibly conceal a small effect.

TABLE 4

Calculated values of the apparent dissociation constants

DROP-RATIO	BROMPHENOL BLUE		METHYL RED		BROMCRESOL PURPLE		BROMTHYMOL BLUE		PHENOL RED	CRESOL RED	THYMOL BLUE
	W*	A†	W	A	W	A	A	A	W	W	W
1:9	4.15	4.33	5.15	4.95	6.31	(6.18)	7.05	7.05	7.78	7.89	(8.96)
2:8	3.98	4.00	4.95	5.02	6.21	6.20	6.98	6.95	7.69	8.04	8.87
3:7	4.06	4.04	5.02	5.06	6.16	6.19	7.05	7.03	7.71	8.04	8.88
4:6	4.01	3.96	5.01	5.03	6.28	6.00	7.04	7.03	7.70	8.10	8.81
5:5	4.02	4.04	4.96	5.01	6.21	6.12	7.04	7.06	7.74	8.08	8.76
6:4	4.03	4.03	4.94	5.01	6.22	6.11	7.05	7.11	7.74	8.12	8.84
7:3	3.93	4.07	4.95	4.97	6.35	6.11	7.10	7.10	7.74	8.06	8.73
8:2	4.07	(4.14)	4.96	4.96	6.29	6.07	7.19	7.10	7.72	8.07	8.82
9:1			(4.90)	4.87	6.14	(6.18)	7.03		(7.64)	7.89	(8.62)
1:4			4.98								
2:3			4.95						7.74		
3:2	4.17					6.26			7.67		
4:1	(4.2)					(6.53)			7.74	8.11	
2:18	4.10	4.05			6.26	6.09		7.07	7.77	8.01	8.82
4:16	4.00	3.97			6.16	6.02			7.69	(8.01)	8.83
6:14				5.01	6.19	6.03		7.09	7.66	8.04	8.84
8:12					6.14	6.03					8.87
10:10		3.90				6.10		7.02	7.72		8.79
12:8						6.09					8.79
14:6		3.91		4.97		6.07			(7.63)	8.08	8.79
16:4		3.84	4.90			6.16		6.97			8.77
18:2		3.94	5.01	4.93		(6.07)		6.92			8.75
Constant.....	4.06		4.96	4.99	6.26				7.72	8.08	8.82
Constant, 10-drop series.....		4.04				6.14	7.06	7.05			
Constant, 20-drop series.....		3.94				6.07		7.01			

* W—Water indicator solution.

† A—Alcohol indicator solution.

Methyl red (4′-dimethylamidoazobenzene-2-carboxylic acid; M. W., 269). There seemed to be no important influence of the alcohol when 10 drops of the alcoholic indicator solution were used. The pipette delivered 48 drops per cubic centimeter. After addition of 10 drops to the buffers the volume was 6.5 cc., and the concentration of absolute alcohol was therefore about 2 per cent.

The temperature coefficient was studied as in the case of bromophenol blue, with the same buffer mixtures. The aqueous indicator solution was used, and the pair having the drop-ratio 2 : 8 was studied. The dissociation constants were calculated by adding 0.60 to the hydrogen-ion exponent values found for the 2 : 8 pair. It should be noted that the constants are not corrected for the change of hydrogen-ion exponent of the buffer mixtures with temperature, and the true variation of the constant with temperature is probably a little greater than would appear from these results. Table 5 gives the results. The value for 18° is one calculated from the data of Tizard.

TABLE 5

Apparent dissociation constant (uncorrected) of methyl red at different temperatures

TEMPERATURE CENTIGRADE	14.5°	18.0°	20.0°	29.5°	40.0°	49.5°
Constant.....	5.13	5.11	5.10	5.05	4.98	4.93

Tizard arrived at the constant 4.98, but the mode of calculation is not suited to present purposes. He came to the conclusion that at most only 93 per cent of the molecules could actually be brought into the red form by an excess of acid and took this into account in the calculation, basing the percentages of color transformed on the theoretical maximal transformation. Now in the present method we must take the actually realizable maximal redness, as obtained by excess (not too great) of acid, as 100 per cent. The writer has therefore recalculated the data of Tizard, taking the maximal redness observed by him as 100 per cent as the basis for calculating the percentage transformed. The results are given in table 6. His results for the more alkaline portion of the range are omitted. The extreme values of the constant given in table 6 deviate from the others, but within the range 10 to 90 per cent transformation the constancy is very good. Neglecting the two extremes, the mean value is 5.11.

TABLE 6

Apparent dissociation constant for methyl red at 18°, calculated from the data of Tizard.

	PER CENT IN THE ACID FORM											
	8.75	11.7	14.3	19.0	22.9	30.6	39.8	47.6	57.9	72.6	86.0	98.5
Apparent constant.....	5.25	5.17	5.12	5.12	5.10	5.09	5.09	5.10	5.11	5.09	5.15	5.86

Propyl red (Dipropylamidoazobenzene-2-carboxylic acid). This indicator has given very good results as used in buffer mixtures, but the colors of the standards are apt to fade prematurely. When the attempt was made to measure the constant the colors in the buffers faded before the measurements could be finished. The equation did not seem to apply at all, but it was observed that after the colors had faded (in the more acid tubes of the buffers) the equation seemed to fit better. This gives a hint that a tautomeric change,

not instantaneous, is involved, but unfortunately this was not followed up at the time. If this is true, the constant would be about 5.28 at 30°. This indicator is not included in the present method.

Bromcresol purple (Dibromo-*o*-cresolsulfonphthalein; M. W. 540). When the alcoholic indicator solution was used a difference in the dissociation constant was noted of 0.12 in the 10-drop series, with a further difference of 0.07 in the 20-drop series. No attempt was made to measure the exponent of the buffer mixtures after addition of alcohol.

TABLE 7

Data for the determination of hydrogen-ion exponent

DROP-RATIO	HYDROGEN-ION EXPONENT FOR EACH PAIR OF TUBES						
	Bromphenol blue	Methyl red	Bromcresol purple	Bromthymol blue	Phenol red	Cresol red	Thymol blue
1:9	3.1	4.05	5.3	6.15	6.75	7.15	7.85
(1.5:8.5)	3.3	4.25	5.5	6.35	6.95	7.35	8.05
2:8	3.5	4.4	5.7	6.5	7.1	7.5	8.2
3:7	3.7	4.6	5.9	6.7	7.3	7.7	8.4
4:6	3.9	4.8	6.1	6.9	7.5	7.9	8.6
5:5	4.1	5.0	6.3	7.1	7.7	8.1	8.8
6:4	4.3	5.2	6.5	7.3	7.9	8.3	9.0
7:3	4.5	5.4	5.7	7.5	8.1	8.5	9.2
8:2	4.7	5.6	6.9	7.7	8.3	8.7	9.4
(8.5:1.5)	4.8	5.75	7.0	7.85	8.45	8.85	9.55
9:1	5.0	5.95	7.2	8.05	8.65	9.05	9.75
Per cent in indicator solution	0.008	0.008	0.012	0.008	0.004	0.008	0.008
Cubic centimeters of 0.1 *N* NaOH per 0.1 gm. portion	1.64		2.78	1.77	3.10	2.88	2.38
Produce acid color with	0.05*N* HCl	0.05*N* HCl	0.05*N* HCl	0.05*N* HCl	0.05*N* HCl	2% H_2KPO_4	2% H_2KPO_4 or H_2O
Quantity of acid used to produce acid color	1 cc.	1 drop	1 drop	1 drop	1 drop	1 drop	1 drop

Bromthymol blue (Dibromo-thymolsulfonphthalein; M. W. 624). This indicator was studied only with its solution in alcohol. When 20 drops were used the constant was different by 0.04, not a large difference in the case of this indicator, the colors of which are not so favorable for exact comparisons as most of the other indicators. The water solution of the monosodium salt will be recommended, and since the constant was found to be 7.01 with 20 drops of alcoholic solution, and 7.05 with 10 drops of the same, we may properly round off the latter value to 7.1, as has been done in table 7.

In a committee report of the Society of American Bacteriologists (8) tests were reported of the value of six pairs according to the technique of Barnett

and Chapman. The technique differed only in that the volume was not kept constant in all the pairs (this should not be of great significance). The values for the ratios from 1 : 9 to 6 : 4, inclusive, were respectively 6.2, 6.4, 6.7, 6.9, 7.1 and 7.3, essentially the same values as reported here.

Phenol red. (Phenolsulfonphthalein, M. W. 354). This indicator is the one studied by Barnett and Chapman, from the ratio 1:9 to the ratio 6:4, inclusive. Their values were 6.9, 7.2, 7.5, 7.7, 7.9, and 8.1, respectively. Calculation shows that all these values lead to very nearly the same value of the dissociation constant, 7.87. In the report of the bacteriological committee already cited, the values reported for these six ratios were 7.1, 7.3, 7.5, 7.7, 7.8, and 7.9. Calculation of the constant yields values varying considerably, the average value, however, being identical with that given by Barnett and Chapman. It is evident that the use of values for the drop-ratios without smoothing out the experimental errors of the calibration would lead to considerable unnecessary error.

In view of the consistent difference between the writer's values and those of Barnett and Chapman (about 0.2 pH) the writer cooled the buffer mixtures (from 29°) to 23° and determined the values of two pairs, and found that the constant was increased by about 0.05 pH. The hydrogen-ion exponents of the phosphate and borate buffers were determined at 27–28° only. Part of the small discrepancy between the results of Barnett and Chapman and those of the writer may therefore be due to the influence of temperature, either on the dissociation constant of the indicator or on the hydrogen-ion exponents of the buffer mixtures. At present there has been published no system of buffer mixtures which has been calibrated at temperatures higher than 20°. Ordinary differences of room temperature are generally neglected in biological work, though of course such neglect may not always be justified. Because the temperature was not specified and the constants only approximately measured for purposes of illustration, the constants given by Clark and Lubs (6) for the various indicators have not been compared with the present values. A number of them differ by about 0.1 or 0.2 from those of the writer, and in the case of phenol red their value is in agreement with those of that of Barnett and Chapman.

Cresol red is ortho-cresolsulfonphthalein, and has the molecular weight 382.

Thymol blue is thymolsulfonphthalein, and has the molecular weight 463. The changes in strong acid solution were not studied.

PREPARATION OF THE INDICATOR SOLUTIONS

At present the indicators are offered in the market both in the solid form, and as solutions of the monosodium salts. The preparation of phenol red offered for a renal function test, containing carbonate, is unsuitable.

The suitable strengths of solution for the preparation of the color standards are given in table 7. The percentages refer to the weight of the free acid indicator. It is understood that precision is not required in the concentration of indicator solution; however, in the preparation of the monosodium salts ordinary care should be observed in the measurement. The quantities of alkali required to form these salts from the solid, free, indicators are given to 0.01 cc. but it is only required to work as well within a tenth of a cubic centimeter as possible.

Although methyl red can be prepared as a monosodium salt in water solution, this is not advised for measurements of the exponents of soil extracts; the alcoholic solution being preferred for reasons given recently (10). The following directions require an analytical balance. Take 20 mgm. of finely ground indicator, dissolve in 150 cc. of alcohol which has been redistilled over a little alkali, and make up the volume to 250 cc. with distilled water. The other solutions required are all made up in water solution. In all cases use a clean mortar (best of agate) and grind up the indicator with the required quantity of standard sodium hydroxide solution, added in portions, at first only moistening the indicator. The required quantity of 0.1 *N* sodium hydroxide solution for 0.1 gm. of indicator is given for each indicator in table 7. These quantities give 1.1 equivalents for each indicator except for bromcresol purple, for which the quantity gives 1.5 equivalents, the stated number of equivalents being required for solution, according to a personal communication from Dr. H. A. Lubs. We generally use 50 mgm. instead of 0.1 gm., using sodium hydroxide more dilute than 0.1 *N* in order to obtain accurate measurement. Heat may be used to effect solution, but should not be necessary. We reported difficulty in avoiding decomposition of bromcresol purple (10) but have had no trouble since that time and believe that the present technique, which is that given by Clark and Lubs (7), avoids all difficulty.

Some of the preparations of indicators on the market are not quite pure, unchanged starting material apparently being present in some brominated indicators. For the preparation and purification of these indicators reference may be made to the work of Lubs and Clark (13, 14) for all but methyl red; and to that of Tizard for methyl red (20). The papers of Acree and his students contain information on this point, for which see reference no. 22 and literature given there. The following notes, obtained from these sources, may be of interest. Bromphenol blue may be recrystallized from glacial acetic acid or (22) from a mixture of acetic acid and acetone; methyl red and bromcresol purple from boiling toluol; cresol red, from glacial acetic acid; and thymol blue, from alcohol.

If the indicators contain impurities having indicator properties, the fact may be disclosed in use by the impossibility of matching the color of the unknown solution by means of any of the color standards.

PREPARATION AND USE OF THE COLOR STANDARDS

The comparator shown in figure 1 is modified from those used by Hurwitz, Meyer and Ostenberg (11) and by Clark and Lubs (6), the principle of which is the same as that of the comparator of Walpole (21). The dimensions are suitable for test-tubes the external diameter of which is a little less than $\frac{5}{8}$ inch, as is the case with those described below. The essentials are that the various holes should lie in the proper planes, as shown by the vertical broken lines. These planes should lie as closely together as possible so that the two optical fields are near together; and the test-tubes should not be too loose in the holes, as otherwise the optical picture may depend somewhat on the position of the tubes in the holes. The view-holes are intentionally smaller than the tube diameter in order to give a homogeneous optical picture, and it is partly for the same reason that the water tubes are inserted. The interior of the comparator is best painted dead black.

Test-tubes of 1.5 cm. external diameter and 15 cm. long are suitable for the comparator illustrated and for the strengths given for the indicator solutions. It is advisable to select from a stock of tubes a sufficient number of uniform tubes by running into each 10 cc. of water and retaining those which are filled nearly to the same height. A variation of 3 or 4 mm. on a height of 8 cm. is permissible. Test-tubes without flanges are preferable. The tubes may be held together in pairs by means of one rubber band per pair, which is wound about the tubes in the form of two figure 8's.

It is convenient to use metal test-tube racks, one for each indicator, each rack holding two rows of tubes, accommodating one tube of each pair in front and one in back. For any desired indicator a set of color standards is prepared by placing from 1 to 9 drops of the indicator solution in the 9 front tubes of the pairs and from 9 to 1 drops in the back row of tubes.[4] A drop of alkali is then added to the tubes in the front row (two drops in the case of thymol blue), sufficient to develop the full alkaline color, and a quantity of acid is added to the tubes of the back row to develop the full acid color without causing a secondary change of color. The quantity of acid to be added varies a little with the nature of the indicator. Table 7 tells the quantity and nature of the acid which can be used without danger of difficulty. If by accident more than one drop is added, no trouble should be caused, and the strengths given need only be approximate. The 0.05 *N* HCl may be prepared by diluting 1 cc. of concentrated hydrochloric acid (sp. g., 1.19) to 240 cc.; and the alkali, by making up a 0.2 per cent solution of stick sodium hydroxide. The volume is at once made up in all the tubes to a constant height (within about one drop) with distilled water, the height corresponding to 5 cc. A different volume may be chosen if desired. A rubber tube with a pinch-cock serves to deliver the water. In making up the volume it is convenient to hold in the

[4] We take the natural precaution of holding the delivery pipette in a vertical and therefore easily reproducible position when adding the indicator drops.

hand a tube containing the chosen volume beside the pair of tubes to be filled. These operations can be carried out rapidly. Investigators may determine for themselves under their working conditions how long the standards may be relied upon to keep. We have found most of them stable for more than two days, and it would appear that no change whatever need be feared during the first day except possibly in the case of cresol red and thymol blue. The ratios given in parentheses in table 7 are secured by the use of a total of 20 drops, distributed 3 drops in one tube of the pair and 17 in the other, and the volume is made double (10 cc.). Such tubes are used in exactly the same way as the others. It will be clear that the ratios 8.5: 1.5, methyl red, and 1.5: 8.5, bromcresol purple are necessary if it is desired to make measurements around the exponent 5.6 as precise as at other points, but the other 20-drop pairs are seldom useful unless some of the indicators are omitted.

If only a few measurements are to be made, it will be desirable to determine what indicators can be used before preparing the color standards. This is readily done in most cases by treating the unknown solutions with the indicators in turn until one of the indicators shows a partial transformation of color. If material is limited this test (or even the actual measurement) may be made by adding 2 drops of indicator solution to 1 cc. of solution. In some cases it may be necessary to use the comparator and a few color standards in order to make sure whether a given indicator can be used or not. When the necessary standards for the needed indicators have been prepared the solution to be examined is treated with 10 drops of indicator solution, such a quantity of the solution being taken in preference that the mixture rises in the test-tube to the height representing a volume of 5 cc. The test-tube containing the mixture is placed in the comparator and its color compared with the color of the standards, any natural color or turbidity of the solution being balanced optically, as shown below. Various color standards are tried, one pair after another, until the color of the unknown is matched with one of the pairs or is evidently between the colors of two of them. In all cases it must be determined that the color is certainly within the range; thus measurements cannot be made at the point where the ratio is 9: 1 or 1: 9, as the percentage transformation of the indicator is so nearly 100 or zero per cent that the hydrogen-ion exponent might really be far from that represented by such a ratio without the fact being disclosed by a color difference. With turbid solutions it may not always be possible to locate the correct ratio when it lies even at 8: 2 or 2: 8. When the ratio has been found which corresponds to the color of the unknown, the hydrogen-ion exponent is found from table 7. Thus suppose methyl red is the indicator used for such a comparison and the color of the unknown lies between the colors of the standards having the ratio 5: 5 and 6: 4, then the hydrogen-ion exponent is found from the table to be between 5.0 and 5.2, or may be put at 5.1, if the color was about as near one ratio as the other. When the color standards are being tried in succession to determine which pair matches most nearly with the fluid of unknown hydrogen-ion exponent it is advisable to take

a simple precaution. If one continues to gaze through the comparator while removing a color standard the color of the tested fluid will appear very strong as soon as the color standard is removed, and this enhancement of color will persist to a noticeable extent when the new color standard is inserted. On this account the change of color standards should always be made without looking through the comparator. It is advisable to make a number of changes of the standards, working rapidly. The eye acquires a temporary sensitiveness of color appreciation.

A good arrangement of the tubes in the comparator for a right-handed operator is the following. Referring to the top view in figure 1, two tubes of water are placed in the two upper left-hand holes and the solution to be examined, treated with indicator, below. The solution without indicator may be placed in the upper right-hand hole, and a pair serving as a color standard in the two lower right-hand holes. It is a natural choice to place the pair so that the color which is dominant is nearer the eye.

The tubes are viewed preferably against the sky. If, in the case of some of the indicators (bromcresol purple, and especially bromphenol blue) a difference of quality appears, due to dichromatism, so that no satisfactory match can be obtained, it will be advisable to view the tubes for the comparison in a yellow light as suggested by Clark and Lubs (6). They use a box containing carbon electric incandescent lamps and the light emerging from the box passes through tracing paper stained yellow by painting it with a mixture of phenolsulfonphthalein (phenol red) (5 cc. of 0.6 per cent solution) and acid phosphate solution (5 cc. of a 3 per cent solution of KH_2PO_4). In using the screened light either white light should be shut off, or at least the arrangement should be such that white light does not enter the eye from one side while viewing the tubes in the yellow light. It is only with very turbid solutions that it is necessary to work with the yellow light.

In using 10 drops of an aqueous indicator solution in a final volume of 5 cc. there is involved a dilution which may in special cases be undesirable. If the solution under examination owes its hydrogen-ion concentration to a strong acid, such a dilution would cause the exponent to be raised by about 0.046, an error not always negligible. This is the greatest error that can be caused by such a dilution when an aqueous indicator solution is used. (We are assuming that 10 drops occupy a volume of 0.5 cc.). If the solution owes its hydrogen-ion concentration to a weak acid the same degree of dilution would cause the exponent to be raised only by about 0.02, while if salts of the weak acid are present the error will be very much smaller. In most biological fluids no error as large as 0.02 is to be expected; with soil extracts it has not yet been determined how nearly the error may approach the maximum, 0.05 pH. If it is desired to reduce the error, each indicator may be used in two strengths, a dilute solution of the strength prescribed above being used for the color standards, and a solution 5 times as concentrated being used for the solution itself, 2 drops being added instead of 10 drops. In the work recently reported in

this journal on soils (10) we used 2 drops of the aqueous indicator solutions to 5 cc. of soil extract, except in the case of methyl red, where 4 drops were used. If the dilute alcoholic solution of methyl red is used in soil extracts, the error due to addition of the alcohol in 10 drops is probably negligible but has not yet been shown so. With methyl red a solution 5 times as strong cannot be prepared in 60 per cent alcohol but one may be prepared 2.5 times as strong as the dilute solution, and 4 drops of this may be used in the soil extract.

A NOTE ON CLEAR SOIL EXTRACTS BY THE USE OF COLLOIDAL IRON

That clear soil extracts can be obtained by the use of colloidal iron is probably known, though the writer is unable to adduce any references, no literature search having been made on this point. The well-known principles of colloidal chemistry apply to the case; namely, in the precipitation of the (negative) colloids by the (positive) colloidal iron the reaction is nearly quantitative, but not to an inconvenient degree, so that practically clear solutions can be obtained with some variation in the proportions of the soil and the colloidal iron. If the iron is added in portions, a larger quantity is required, also a slight excess of iron may be caused to disappear by again shaking up the soil with iron.

A commercial "dialyzed iron" was found to contain enough acid to affect somewhat the hydrogen-ion exponent of the extracts obtained by its use. Although the addition of silver nitrate did not cause precipitation (at least immediately), an immediate change was easily visible upon examination by reflected sunlight through the side of the test-tube. On dilution the solution showed a high acidity against methyl red. After removal of the iron by addition of ammonia and boiling, a strong test for the chlorine ion was given with silver nitrate in the presence of dilute nitric acid. The preparation contained 7.5 gm. of solids in 100 cc. Gravimetric analysis showed a ratio, Fe_2O_3:AgCl, equal to 2.9. The variations in the formula for the "oxychloride" of dialyzed iron given by the United States Dispensatory (19th edition), on the authority of Graham, correspond to variations in this ratio of 2.4 to 8.8.

A quantity of the commercial preparation was redialyzed in a thin collodion bag in running distilled water, the velocity of which was increased about the bag by putting it in a tube of only slightly greater diameter. The dialysis continued two days and the ion did not precipitate in this time. Water entered during the dialysis, causing a dilution of about 25 per cent. The redialyzed product was found to have lost but very little of its precipitating power for soils. When it was diluted, two drops to 10 cc., and attempts were made to determine its hydrogen-ion exponent, methyl red gave the exponent 4.8; and bromcresol purple, a very different result, 6.2. Analysis showed the ratio Fe_2O_3: AgCl, equal to 6.4.

This redialyzed iron was used to obtain clear soil extracts for the measurement of hydrogen-ion exponent in the following way. To 30 cc. of distilled water in a wide test-tube, 15 gm. of the air-dry soil were added, the tube

closed and violently shaken 50 times. The dialyzed iron solution was added and the whole immediately shaken a few times to mix thoroughly. On standing, if the proper quantity of iron had been added, the soil particles began at once to subside and soon left a perfectly clear extract above, save for a few floating particles around the edge of the surface. If not quite enough iron was added, fine white suspended particles could be seen, which did not interfere with the measurements. Excess of iron, which is shown by the color of the suspended particles, was carefully avoided, as this had already been found to yield results more or less too acid. The clear fluid was drawn off in a pipette well rinsed with distilled water and the hydrogen-ion exponents determined by the technique given in this paper. The results are given in table 8, together with the results which had previously been obtained for the given soils colorimetrically, by the use of a centrifuge (without iron) and buffer mixtures, and also electrometrically. The first seven soils were Caribou loam and the last two Washburn loam.

TABLE 8

Hydrogen-ion exponents measured for some soils by the use of the colloidal iron method of clearing, compared with the results obtained by the usual methods

SOIL	QUANTITY OF IRON SOLUTION ADDED	HYDROGEN-ION EXPONENTS		
		Iron method	Centrifuge method	Electrometric method
1	8 drops	4.55	4.5	4.50
2	8 drops	4.9	4.9	4.64
3	7 drops	4.8	4.8	4.80
4	9 drops	4.95	4.75	4.80
5	6 drops	5.05	5.0	4.90
6	2 cc.	5.0	5.0	5.00
7	2 cc.	5.2	5.0	5.00
8	1 cc.	5.65	5.6	5.68
9	12 drops	5.8	5.7	5 75

In the case of the Caribou and Washburn loams listed in table 8 the extracts prepared with iron gave practically the same results as did those obtained with the centrifuge (and of course without iron). Those obtained with iron are also far clearer than can ordinarily be obtained with a centrifuge of usual power. A heavy red (Susquehanna) clay, not air-dried, suspensions of which could not be cleared sufficiently with a centrifuge to permit any measurement of hydrogen-ion exponent, gave a water-clear extract by the use of a small quantity of iron solution. The use of iron would be of especial use in the case of fresh soils, which are more "colloidal" than after air-drying.

Nevertheless, the writer does not feel justified in proposing such clearing with iron for the measurement of hydrogen-ion exponent, on the ground that other soils, with possibly smaller "buffer action," might possibly be changed by the residual acidity of the colloidal iron used. It is not supposed that colloidal iron can really be prepared entirely free from acid. It is supposed to

be a mixture, in varying proportions, of oxychloride and hydrate. The hydrate of the mixture does not, however, show the same solubility relations as does freshly precipitated hydrate. Although the ratio, Fe_2O_3: $AgCl_2$, for a given preparation would serve in some degree to specify the degree of dialysis, it would appear that considerable more work would have to be done on the subject in order completely to specify the properties necessary for obtaining reliable results. It may, however, be well worth while for those who can check the results for different types of soil, either electrometrically or colorimetrically by the use of a centrifuge, to test the applicability of the method for themselves.

SUMMARY

A simple technique has been described in full for the preparation and use of a series of color standards for the colorimetric determination of hydrogen-ion exponent. No buffer mixtures are required. From the method of calibration, however, any salt or protein errors will be the same as if the measurement had been made with the 0.05 *M* buffer mixtures of Clark and Lubs.

Each color standard consists of two test-tubes, one tube containing dilute alkali and the other dilute acid. The tubes contain altogether 10 drops of indicator solution, the ten being divided between the alkaline and the acid tubes in various "drop-ratios."

A table is given (table 7) containing all the necessary data.

The method is based on a study of the nature of the color change of the indicators with change of hydrogen-ion exponent (pH). For all the indicators selected the following equation, which comes from the mass action law, was found to hold within the experimental error of the color readings:

$$\text{pH} = k + \log (\text{drop-ratio}).$$

The indicators studied are from the selection of Clark and Lubs; and the values of the constant k of the equation, good to about 0.1 at 25–30°, are as follows: bromphenol blue, 4.1; methyl red, 5.0; bromcresol purple, 6.3; bromthymol blue, 7.1; phenol red, 7.7; cresol red, 8.1; and thymol blue (alkaline range), 8.8.

Soil extracts were prepared, water-clear, by the use of colloidal iron solution. Measurement of the hydrogen-ion exponents of these extracts (from nine soils only) gave the same results as were obtained by the usual methods. Without further study, however, such use of colloidal iron cannot be recommended for general use.

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THE COMPARATIVE RATE OF DECOMPOSITION OF GREEN AND CURED CLOVER TOPS IN SOIL

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INTRODUCTION

The rate of decomposition of leguminous crops is becoming an extremely important practical question in soil fertility and crop production. The rate of nitrate production is the most important phase of this subject, bearing directly upon the value of the crop for soil improvement either in the green or in the cured condition. Two methods have frequently been employed for measuring the rate of decomposition of organic materials such as occur in nature. One consists in measuring the carbon dioxide production at various intervals; the other is concerned with the determination of nitrate nitrogen at various periods. This latter method is superior in most cases, as it is possible to determine the actual amounts of nitrate nitrogen present, the amount used by the crop, and that lost by leaching. It furnishes data on the nitrogen requirements of the plants at critical periods. The importance of the element nitrogen and the changes occurring in the nitrogen cycle demand more consideration than the changes occurring in the carbon cycle, owing to the solubility, expense and amount of the element nitrogen required for crop growth. There has been no method developed that indicates that there is a true ratio between the amount of carbon oxidized and the amount of nitrogen oxidized. That such a ratio may exist at certain times for some crops cannot be denied, but the fact that non-nitrogenous materials constitute a large proportion of most of the materials that are used for soil enrichment and that the ratio of carbon to nitrogen is constantly changing with maturity, is sufficient evidence to indicate clearly the wisdom of studying the nitrate production in preference to that of carbon dioxide.

Red clover and sweet clover (*Melilotus alba*) are seeded in small grains, usually in the winter or early spring, to be plowed under the following year, either green or after a seed crop has been taken.

It will be evident that any condition which may be found or that can be created that will insure ample nitrate nitrogen from a leguminous crop plowed under as manure for the succeeding crop of that year, will assist materially in increasing crop yields and in eliminating nitrogen as a limiting element.

Furthermore, it will be just as obvious that a retarded nitrate nitrogen production, which fails to supply nitrate at the critical periods in the growth of the crops, but which may supply large amounts later, will tend to result in wasteful losses through leaching, and not infrequently in delayed growth and maturity of the crop. The importance of controlling the rate of nitrate production is such as warrants extended study of this subject.

This paper is a contribution to that phase of the subject of the decomposition of leguminous crops that is concerned with the comparative rate of decomposition of common red clover tops, when employed as a manure, in the green and in the cured condition.

HISTORICAL RÉSUMÉ

Only a few articles have been found in the literature which have a bearing upon the particular phase of the subject under study.[1] Potter and Snyder (3) studied, in one case only, the decomposition of green clover and compared it with the decomposition of some dry clover in another experiment. While a direct comparison is not available, their results indicate a more rapid production of carbon dioxide in soil treated with the green clover than in that treated with air-dried finely-ground clover. This work is in accordance with other experiments in regard to the rapid initial decomposition that takes place with green manures. No study was made of the nitrogen in the materials and therefore the work is not of assistance in estimating the comparative production of nitrates.

Boltz (1) reported two experiments in which green clover incorporated with the soil was compared with green clover allowed to remain on the surface, and found more decomposition had taken place with the clover on the surface than when incorporated with the soil. This experiment furnishes valuable information in connection with fall plowing of crop residues compared with leaving them on the surface. It is rather surprising to find such a large decomposition of carbonaceous material with no apparent loss of nitrogen. The amount of carbon represented as lost with no nitrogen loss indicates clearly a decomposition of non-nitrogenous constituents of the material or only a partial transformation of the nitrogen contained. If the experiments had extended through the period of most active decomposition which occurs usually in late May and June, no doubt entirely different results would have been obtained. It suggests the desirability of more investigation along this line.

Hutchinson and Milligan (2) studied the decomposition of a legume crop in the green condition, and after drying for 24 and 48 hours, in connection with the rate of ammonia, nitrite and nitrate production. This work is

[1] The work reported in this publication was completed in 1916 but publication was delayed on account of the war. An article published by J. W. White (Soil acidity as influenced by green manure. *In* Jour. Agr. Res., 1918, v. 13, p. 171–197) supports the data herein reported as regards the rate of decomposition of green and air-dried materials.

pertinent to the data presented by the authors of the present article. The legume used by Hutchinson and Milligan was *Crotalaria juncea* and the samples were cut from plantings four weeks old. This young succulent growth possessed a moisture content of 452.1 per cent on the water-free basis, or 81.8 per cent of the green material. The results in table 1 are taken from their bulletin.

By calculating from the authors' data, it will be found that the total inorganic nitrogen transformed was 68.1 per cent, 57.3 per cent, and 47.1 per cent, for the crop buried immediately, that buried after drying for 24 hours, and

TABLE 1

Effect of drying green crop before burial

TREATMENT*	NITROGEN DETERMINED	NITROGEN PER 100 GM. SOIL						
		1 week	2 weeks	3 weeks	4 weeks	6 weeks	8 weeks	12 weeks
		mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*
Buried immediately	Ammonia	6.9	2.5	1.0	2.0	1.0	2.0	2.0
	Nitrite	1.2	0.01	nil	nil	0.01	0.01	0.02
	Nitrate	3.1	6.9	8.4	8.9	9.4	9.8	8.7
							68.0%†	
Buried after drying for 24 hours	Ammonia	6.5	3.5	2.5	3.5	3.5	3.5	2.0
	Nitrite	1.1	0.02	0.02	nil	0.02	0.03	0.02
	Nitrate	4.1	5.1	6.0	6.9	6.9	6.9	6.5
							45.3%	
Buried after drying 48 hours	Ammonia	5.4	3.5	4.0	4.0	2.5	3.0	2.5
	Nitrite	0.05	0.02	0.03	nil	0.02	0.03	0.02
	Nitrate	3.8	5.1	5.3	5.3	5.4	6.1	5.8
							39.1%	

* 12.8 mgm. of nitrogen were added in green material per 100 gm. of soil.

† Per cent nitrified of organic nitrogen added.

that buried after drying for 48 hours, respectively. When, however, the nitrate alone is considered the differences are much greater in favor of the "buried immediately" material. The production of ammonia was somewhat greater with the treatments which had partially dried. The presence of nitrite for the first seven days is of considerable importance to note, as the amount is sufficiently high to be injurious to most vegetation.

Another point of interest that appears throughout the whole work of these investigators is that the maximum nitrate production was found to occur at the eighth week from the time of burial.

EXPERIMENTAL METHODS

The experiment reported in this paper was planned with the object of making a comparative study of the rate of decomposition of red clover tops, turned under green and cured by drying, all other conditions and factors being the same in both cases. The rate of decomposition was studied by experiments conducted in both the laboratory and the greenhouse. The main points considered were the transformation of the nitrogenous compounds, loss of carbon, and the effect upon growing crops planted at various periods after the beginning of the experiment.

General plan

The experiment was conducted in parallel in the greenhouse and in the laboratory. Twelve 1-gallon earthenware jars were prepared for the greenhouse experiment; four containing the soil alone, four a mixture of the soil and green clover tops, and four a mixture of the soil and cured clover tops. Two jars of each treatment were selected to draw samples from, for the analytical work, and the other two were reserved for growing oats. In order to make the chemical determinations more accurate, it was necessary to make a rather heavy application of organic matter. Consequently, the clover was applied at the rate of 50 tons of green manure per two million pounds of soil. In the laboratory experiment ½-pint jelly glasses, covered with tin lids in which a small hole had been punched, were used for containers. Sixty glasses were prepared, twenty for each of the above mentioned treatments. The applications of organic matter were approximately twice as much as in the 1-gallon jars.

The additions of green and cured clovers were in equivalent amounts; that is, the loss of moisture in curing was determined and the applications were made so that every jar received the same amount of organic matter. At the time the clover was mixed with the soil, the cured-clover-soil mixture was moistened with sufficient distilled water to bring it to the same moisture content as the green, thus both treatments were uniform with respect to moisture content.

Materials used and their preparation

The soil used was a heavy phase of brown silt loam. The clover was of a late fall growth, and represented both young and old plants, some which were large and woody with dried-up blossom heads. The original sample was thoroughly mixed and divided into two portions of 1500 gm. each. One portion was spread out thinly on a sheet of cheesecloth and dried for three days in the breeze from electric fans. In the three days of curing the weight of the clover decreased to 441 gm. The other portion was stored in shallow trays in a refrigerator at a temperature a few degrees above the freezing point. The green clover weighed 1504 gm. when removed from the refrigerator. Both lots were cut into pieces of approximately ½ inch in length.

Details of greenhouse experiment

Three lots of soil weighing 16 kgm. each were placed in piles on the greenhouse bench. To one lot was added 720 gm. of the chopped green-clover tops; to the second 211.6 gm. of chopped, cured-clover tops and 508.4 gm. of distilled water. The added materials were thoroughly mixed throughout the whole soil mass. To the third lot of soil no addition was made, but it was subjected to the same mechanical treatment as in the other cases. Four 1-gallon jars were filled with each mixture and four with soil alone, each jar receiving a total of 4000 gm.

The soil used was obtained directly from the field and when collected, contained an optimum moisture content; consequently no water was added except in cases where a deficiency resulted due to handling or where rapid evaporation from the green clover occurred. The total weights of the jars were recorded and they were periodically brought up to the original weight by the addition of nitrogen-free distilled water. The original moisture content was lowered somewhat as decomposition progressed, because of the larger amount of available moisture resulting from decreased capacity for absorption. The soil in these jars was cultivated and thoroughly stirred after each sampling. On the third day after starting the experiment one jar of each treatment was planted with 16 selected seeds of Silver Plume oats, and on the twenty-first day, another jar of each treatment was planted with 20 selected seeds of the same variety.

Details of laboratory experiments

In each of the sixty jelly glasses was placed 120 gm. of the same lot of soil as that used in the greenhouse experiment. The first twenty received in addition 10 gm. each of green-clover tops, which had been chopped as previously described. To the next twenty glasses were added in a similar manner 2.93 gm. of cured-clover tops and 7.1 gm. of distilled water. The remaining twenty glasses served as checks. The glasses were all weighed and whenever necessary enough water was added to restore them to their original weight. They were cultivated after each watering. These treatments were incubated at room temperature in the laboratory. In order to test the effect of a limited supply of oxygen on the decomposition, four shaker bottles were added to the experiment. In the first two were placed 120 gm. of soil and 10 gm. of green-clover tops, while the other two received 120 gm. of soil, 2.93 gm. of cured-clover tops and 7.1 gm. of distilled water. These bottles were stoppered tightly and incubated at room temperature for seven months. The details of the experimental plan are arranged in table 2.

Sampling and analytical methods

In sampling, the whole of the contents of the jars in the greenhouse was stirred with a large spatula and then an equal weight of soil was taken from each of two jars of the same treatment. The soil was then mixed together, making a composite sample of the same treatment from two jars. In the laboratory the total contents of two jelly glasses from each treatment were mixed in the same manner as the samples from the jars. Samples were taken in this manner to avoid, as much as possible, individual differences among the containers.

Moisture determinations were made by drying in the electric oven at 110°C. in the usual manner. Ammonia nitrogen was determined in duplicate on all

TABLE 2

Details of experimental plan

TREATMENT	SOIL	CLOVER	WATER	MOISTURE PRESENT	CLOVER ADDED	NITROGEN ADDED	TOTAL NITROGEN PRESENT
Materials used in four jars							
	gm.	*gm.*	*gm.*	*per cent*	*p.p.m.*	*p.p.m.*	*p.p.m.*
Greenhouse:							
Soil and green clover	16,000	720.0	0	33.00	14,163	497.1	4,084
Soil and cured clover	16,000	211.6	708.4	33.00	14,163	437.8	4,036
Soil alone	16,000	0	308.0	29.87	0	0	3,522
Material used per glass							
Laboratory:							
Soil and green clover	120	10.0	0	33.25	25,215	885.6	4,331
Soil and cured clover	120	2.93	7.1	33.25	25,662	792.0	4,236
Soil alone	120	0	4.0	30.38	0	0	3,535

of the samples by aeration with magnesium oxide at room temperature. This method was first developed in this laboratory. Since this work was completed, results showing the value of magnesium oxide in aeration methods for ammonia determinations in soils have been published from the Ohio Experiment Station and therefore need not be repeated here.

For the nitrate determinations

The dried soil was put into 400-cc. shaker bottles and 300 cc. of hydrochloric acid (5 cc. of concentrated acid in a liter) were added to each bottle. The bottles were then shaken 20 minutes, and then allowed to settle over night. Two hundred cubic centimeters of the supernatant liquid were removed and placed in Kjeldahl flasks. Six cubic centimeters of potassium hydroxide solution (600 gm. per liter) were added and the ammonia expelled by boiling

almost to dryness. One gram of Devarda's alloy was added to each flask together with 250 cc. of water. The distillation was carried out in the usual manner. Rosolic acid was used as the indicator in titrating.

The total nitrogen and total carbon were determined on the air-dried samples by the Kjeldahl and sodium peroxide fusion methods, respectively. Slight differences were found between the nitrogen content of the green and cured clover tops. The differences were not, however, sufficient to affect the determinations. The slightly lower nitrogen content of the cured clover is unaccountable, but similar results have been observed by other investigators.

EXPERIMENTAL RESULTS

Table 3 shows the ammonia and nitrate content of the various treatments at different periods in the progress of the greenhouse experiment. The figures show that the decomposition of both kinds of clover was fairly rapid. The maximum ammonia content was found at the beginning of the experiment. There was a gradual decrease to about the normal production for the brown silt loam soil. There was not the slightest indication of a very rapid accumulation of ammonia in the early days of the experiment such as has been found repeatedly in this laboratory with green alfalfa or dried blood. The difference in ammonia production between fresh and cured clover is not such as to indicate anything of value regarding the rate of decomposition of the two materials. This, of course, was to be expected in a soil of this type. Ammonification is not an index as to the rate of decomposition. The production of nitrate from the fresh clover proceeded rapidly from the beginning, and continued well in the lead for two months over the production from the cured clover. On the eighty-ninth day the nitrate content of the two treatments was practically the same, and on this date also both treatments showed a maximum increase in nitrate over the soil alone. The proportion of the original nitrogen added transformed into nitrate for the fresh clover was 31.34 per cent, and for the cured, 34.35 per cent.

It is to be noted that the important differences occurred during the first eight weeks. This more rapid decomposition on the part of the green material is an important consideration, particularly in connection with a crop such as corn, which is planted after the plowing under of a green manure about the first of May. If differences of this kind occur between fresh and cured clover, such as that used in the experiment, it is reasonable to assume that much greater differences would occur with clover which had been subjected to longer curing. Curing appeared to have a retarding effect in the early stages of decomposition, but the effect was not noticeable after two months.

The results obtained in the laboratory are shown in table 4. The largest content of ammonia was found in the green-clover treatment at 10 days. Because of the larger amount of material used in the laboratory experiment, a much greater accumulation of ammonia was to be expected, especially with

the green clover. The amount found, however, is only about 9 per cent of the nitrogen applied in the case of green clover and less than 3 per cent in the case of cured clover at 10 days, when the maxima occurred. At 10 days the green clover was still higher than the cured, but from that time on there was little difference between the two treatments. The results of the nitrate determinations are much more striking than those of the ammonia. The green clover produced nitrate very rapidly with a maximum transformation of 35.8 per cent of nitrogen added after 43 days. The cured clover produced nitrate more slowly; only 15.7 per cent of the nitrogen applied was found in the form of nitrate at the end of 43 days.

The maximum nitrate accumulation for the cured clover occurred at 152 days when 24 per cent was nitrified. The largest actual amount of nitrate

TABLE 3

Ammonia and nitrate nitrogen content of soil treatments at different periods in greenhouse experiment

TREATMENT	NITROGEN AS PARTS PER MILLION OF WATER-FREE SOIL								
	0 days	10 days	18 days	30 days	43 days	59 days	89 days	152 days	213 days
Ammonia									
	p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*
Soil and green clover	23.9*	21.7	14.0	11.3	15.6	13.1	4.6	13.5	7.5
Soil and cured clover	27.8	17.6	7.5	3.9	21.9	9.6	4.9	13.8	8.6
Soil alone	9.4	9.6	6.3*	4.3	8.6	6.3	3.1	—	5.6
Nitrate									
Soil and green clover	10.2	80.4	101.1	112.3	102.5	122.3	197.8	163.4	203.7
Soil and cured clover	10.6	56.1	85.4	83.1	93.8	103.9	192.4	84.4*	178.4
Soil alone	9.4	36.6	32.8	24.8	24.9	24.6	42.0	43.5	51.6

* Single determination; all the others are averages of duplicates.

found was 347.1 parts per million, and whenever the nitrate approached this amount, a drop occurred followed by another approach to the maximum. This was thought to be due to a sufficient concentration of the nitrate to inhibit biological action, but upon calculation it was found that this could not be a factor, and it appears that an equilibrium may occur between protein formation and nitrification when the maximum is reached. This equilibrium may be broken by protein formation exceeding nitrification, and vice versa. Total nitrogen determinations gave no evidence that denitrification was taking place. The effect of curing on ammonification was of no importance, but a very marked effect was observed on nitrate production. This effect was much greater in the laboratory experiment than in the greenhouse experiment. Although almost the same maximum percentage of nitrate production was found from both the fresh and the cured clover, the attainment of this max-

imum was delayed 109 days by the curing in the laboratory experiment. Whether the difference between the laboratory and the greenhouse experiments was due entirely to the different rates of application of the clover or to some other influences cannot be told from the data at hand. It is evident that both methods are sufficient to indicate the direction the decomposition takes, and data obtained by these methods are perhaps as reliable as the results obtained under field conditions. The data do not indicate that the kind of decomposition in the case of the fresh and cured material was essentially different. The per cent of nitrogen changed to nitrate was almost the same in both laboratory and greenhouse methods. This per cent was not influenced by the curing or by the rate of application.

TABLE 4

Ammonia and nitrate nitrogen content of soil treatments at different periods in laboratory experiment

TREATMENT	NITROGEN AS PARTS PER MILLION OF WATER-FREE SOIL								
	0 days	10 days	18 days	30 days	43 days	59 days	89 days	152 days	213 days
Ammonia									
	p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*
Soil and green clover	48.9	89.6	34.8	13.5	21.5	14.6	3.2	19.2	5.4
Soil and cured clover	36.1	36.7	20.0	14.0	20.0	17.8	8.6	19.1	8.4
Soil alone	9.6	8.1	2.7	8.1	7.0	8.7	5.8	7.5	3.7
Nitrate									
Soil and green clover	10.0	95.9	206.0	269.6	347.1	338.9	300.5	289.6	326.7
Soil and cured clover	10.0	71.2	114.4	130.8	154.7	197.4	266.8	332.9	309.0
Soil alone	9.4	18.0*	26.1	24.5	30.2	49.2		63.4	66.0

* Single determinations; all the others are averages of duplicates.

Decomposition in presence of a limited supply of oxygen

The senior author had occasion to observe a very acid decomposition of green vetch which appeared to be due to an excess of moisture. In order to test the possibility of clover producing the same kind of fermentation, both green and cured clover were subjected to conditions of a limited supply of oxygen by incubation in stoppered shaker bottles as described above. The decomposition under these conditions was found to be widely different. In table 5 are included the ammonia and nitrate results.

The high accumulation of ammonia with the green clover is sufficient under normal conditions to stop nitrate production in this soil, but not sufficient to stop nitrite formation. The cured clover produced a large amount of nitrate and actually consumed in so doing about 66 per cent of the available oxygen. The green-clover treatment possessed the odor typical of silage and

was extremely acid. It should be observed that this is not a case of denitrification, but a case of an acid fermentation in which the initial stages of ammonification were not inhibited. It suggested that an acid fermentation may result under field conditions when the green decomposing material is in any way sealed up by water or by a blanket of carbon dioxide in the soil. Further work will be conducted along these lines, as it appears that this condition is not infrequently met with in wet seasons, and is a probable cause of injury to crops planted after plowing under heavy growths of green manures. The stems and leaves were in a fair state of preservation after 7 months in these treatments, while under more open conditions only small portions of the woody stems were found.

TABLE 5

Ammonia and nitrate nitrogen produced by green and cured clover with a limited oxygen supply

Duration 213 days

TREATMENT	NITROGEN	
	Ammonia	Nitrate
	p. p. m.	*p. p. m.*
Soil and green clover	224.9	6.0
Soil and cured clover	106.6	97.2

Loss of carbon

The loss of carbon during 152 days of the experiment is reported in table 6. While there is a relatively large error in the total carbon determinations, nevertheless these results show distinct decreases in the carbon, and in all cases the green clover lost considerably more than the cured.

TABLE 6

Loss of carbon during 152 days of decomposition

TREATMENT	CARBON LOST
	p. p. m.
Greenhouse:	
Soil and green clover	2456
Soil and cured clover	2214
Laboratory:	
Soil and green clover	8218
Soil and cured clover	5857

Carbon and nitrogen relationships

The ratio of total carbon to total nitrogen, and the ratio of carbon lost to nitrate formed, are given in table 7 in order to show the rapid narrowing that occurred in a relatively short time, and to further point out the fact that the

carbon-nitrogen ratio of the green-clover treatment narrowed faster than that of the cured-clover treatment. The ratio loss of carbon to nitrate formed was much greater with the green-clover treatment than with the cured-clover treatment. These ratios represent quite accurately the relative rates of decomposition of the two materials and the relative rates as they occurred in the two experiments. The carbon-nitrogen ratio indicated that the green clover had reached a more advanced stage of decomposition than the cured clover.

TABLE 7

Carbon and nitrogen relationships

TREATMENT	RATIO OF CARBON TO NITROGEN		RATIO OF CARBON LOST TO NITRATE FORMED
	0 days	152 days	C to N
	C to N	C to N	
Greenhouse:			
Soil and green clover	12.4–1	11.7–1	12.3–1
Soil and cured clover	12.4–1	11.8–1	11.5–1
Laboratory:			
Soil and green clover	12.8–1	10.9–1	23.6–1
Soil and cured clover	12.6–1	11.1–1	17.6–1

Effect of decomposition of green and cured clover on oats

One jar of each treatment was planted with Silver Plume oats 3 days after the experiment was started and 21 days after starting, a second planting was made in three other jars. The oats from the first planting were up after 4 days. Injury in the germination was noticeable where the organic matter was present and it was greater with the green clover. Only 6 seeds out of 16 germinated at all and these very poorly where the green clover had been applied, while 10 germinated where the cured clover was applied and 16 in the soil check. For about two weeks the plants in the green-clover treatment were much behind those in the other treatments, but gradually the differences disappeared. The oats were germinated at a time when the temporary ammonia accumulation from the green clover might account for the injuries observed. No injuries were observed with the oats planted 21 days after the applications were made. In both cases at the close of the experiment the green and cured treatments were ahead of the checks.

DISCUSSION

Hypothetical reasons for differences in rate of decomposition between green and cured clover

In considering the greater initial rate of decomposition exhibited by the green clover as found by all methods used to study the decomposition, it did not appear that there were any indications of purely chemical changes having occurred in the clover during dehydration. Enzymic action as a factor in affecting the cell contents is not an impossibility, but the temperature at which the green clover was held during the dehydration of the lot with which it was compared, would exclude the possibility of much change in it, while the dehydration process with the other lot of clover would require the action of the synthetic enzymic processes to retard its rate of decomposition by stabilizing the nitrogen compounds.

The explanation that seems to fit the results found is based on a physical hypothesis. The loss of water is of course accompanied with an increase in the concentration of salts in the cells. This brings about a hardening of the cell contents, and the whole material becomes more horny and shriveled. The diffusion of nitrogenous substances is stopped until hydration has been reestablished. The colloidal nature of the cell contents causes them to become hydrated slowly, after a previous dehydration. Apparently the time required to bring about the hydration in a normal soil is sufficiently long for the ammonifying bacteria to gain headway on the green material, and consequently to effect a much greater rate of decomposition than those acting on the dehydrated material.

CONCLUSIONS

1. The comparative rate of decomposition of green and of cured red clover tops was studied in soil. Curing retarded the rate of decomposition as measured by ammonification, nitrification and loss of carbon in both laboratory and greenhouse experiments. The green clover produced nitrate very rapidly, with a maximum transformation in the laboratory experiment at 43 days of 35.8 per cent, while with the cured clover at the same period only 15.7 per cent of the nitrogen had been transformed. In the greenhouse experiment the green clover was well in the lead in nitrate production during the first two months.

2. Green and cured red clover underwent the same kind of decomposition under aerobic conditions.

3. With the oxygen supply limited, the types of decomposition of green and cured red clover were vastly different.

4. There was no measurable loss or gain of nitrogen during the experiment.

5. The loss of carbon, and the change in the carbon-nitrogen ratios agreed with the other determinations in showing a difference in rate of decomposition between the green and the cured clover, but did not indicate a difference in kind.

6. The change which dehydration (curing) brought about in the rate of the initial decomposition appears to be of a physical nature only. An explanatory hypothesis is that dehydration resulted in a hardening and shriveling of the tissues which interferes with the reentrance of water and consequently delays the decomposition because the bacteria must await the softening of the tissues before they are able to start their work, while with the green no such delay occurs, as the cells are already hydrated.

7. Planting oats 3 days after treating the soil with green and cured clover resulted in serious injury which delayed growth. It was greater with the green clover.

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CONCERNING THE EFFECT OF HEAT ON THE REACTION BETWEEN LIME-WATER AND ACID SOILS

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Lime-water (calcium hydroxide) added to so-called "acid soils" as an index of the lime requirement, has been generally employed by analysts since Veitch (5) outlined his method in 1902. Many workers throughout the country consider the method superior to any other as an indication of the total lime requirement of a soil and advise treatment accordingly. In scientific investigations of soil problems pertaining to soil acidity and general fertility, the method is often used to show various changes that have occurred. Whenever a new method for soil acidity or lime requirement has been suggested the Veitch lime-water method is usually taken as a means of comparison. A similarity of results is often considered desirable. In view of these conditions it is important that we have as complete a knowledge as possible of all factors that would influence the results obtained by the method in question.

During the course of an investigation pertaining to the acid condition of Oregon soils it was observed that the lime requirement of an acid soil, as indicated by the Veitch (5) lime-water method, was greater after treatment with limestone than before treatment. Since the first determination was made on a hot-water bath while the later one was carried out on a sand bath heated by a coil of steam pipes, it was thought that the degree of heat or manner of evaporation might be an important controlling factor and account for the inconsistent results. Accordingly, a study was made to ascertain the various conditions that affected the lime requirement as shown by results of the lime-water method.

Five acid soils, widely different both physically and chemically, were used in the investigation. A physical classification as shown by a mechanical analysis is as follows:

No. 11076	Silty loam
No. 11077	Gravelly loam
No. 11078	Williamette silty loam
No. 11079	Clay loam
No. 11080	Medium sandy loam

The soil samples were air-dry, and, except for a limited amount of grinding with a rubber-tipped pestle, were used as obtained from the field.

In all determinations of the lime requirement the procedure was followed as recommended by Veitch (5). The quantity of soil used each time was 10 gm. Water was first added to the soil to make the final amount 65 cc. after the standard lime-water was added, except for those soils having an abnormally high requirement. Evaporations were then carried on, as will be described later. After drying, the soils were taken up with distilled water and transferred to 250-cc. centrifuge bottles, 75 cc. being the total amount of water used. The bottles were shaken occasionally during 3 hours of the afternoon and allowed to stand over-night. Instead of decanting through filter paper, the bottles were placed into a centrifuge and whirled at the rate of about 2400 revolutions per minute until a clear solution was obtained. After the addition of phenolphthalein indicator, 50 cc. of this solution was

TABLE 1

The effects of heating on the lime requirements of a soil by the Veitch method

AMOUNT TAKEN	METHOD OF EVAPORATION	TEMPERATURE	TIME FOR EVAPORATION	LIME REQUIREMENT ($CaCO_3$ FOR 2,000,000 POUNDS OF SOIL)
gm.		°C.		*lbs.*
10	On steam bath	100	1.0 hr	2600
10	On steam bath	90	1.5 hr.	2150
10	On steam bath	70	2.5 hr.	1300
10	On steam bath	100	1.0 hr.,—left 10 min. after dehydration	3200
10	On steam bath	100	1.0 hr.,—left 20 min. after dehydration	3400
10	In vacuum oven	75	About 20 hr.	3900
10	In vacuum oven	60	About 8 hr.	1700
10	In vacuum oven	60	About 10 hr.	2150
10	On hot plate	Low heat	2 hr.	4300
10	On sand bath	110	About 8 hr.	4600

then boiled until the appearance of the pink color, or, in case no color developed, to about 5 cc. Care was taken to maintain the above conditions in order that the ratio of soil to water would be constant in all determinations and to control other influencing factors. Control determinations were run to ascertain any alkalinity that might develop from the use of the glass apparatus. The 200 cc. of the distilled water evaporated down to 5 cc. in the Pyrex beakers used gave no trace of alkalinity to phenolphthalein indicator.

Soil 11078 was selected for a detailed study pertaining to the effect of heat during the process of determining the lime requirement by the Veitch method. This soil type gave a distinct acid reaction to litmus paper and had a lime requirement of 1 to 3 tons per 2,000,000 pounds of soil, depending upon the laboratory method used for the determination. It does not, however, respond to lime treatment, as indicated by crop production. Evaporations of the treated soil were conducted on a hot-water bath (called steam bath by

Veitch) at different temperatures controlled by gas burners; on a sand bath heated by steam coil pipes; on a hot plate at "low heat" connections; and in a vacuum oven at various degrees of temperature controlled by gas burners. Table 1 gives the lime requirement as indicated by the conditions under observation. The results are reported as pounds of calcium carbonate per 2,000,000 pounds of soil.

These results show a wide variation in the lime requirement of an acid soil, depending upon the manner of evaporation after treatment with standard calcium hydroxide. When the evaporation was conducted on the steam bath highest results were obtained at a temperature of 100°C. Any decrease in temperature showed a corresponding decrease in the lime requirement. At a temperature of 70° the lime requirement was 1300 pounds, while at 100° it was 2600 pounds, or 100 per cent higher. Furthermore, if the treated soil was allowed to remain on the steam bath 20 minutes after evaporation to dryness was completed, the lime requirement was 3400 pounds, or almost three times as much as was indicated when the treated soil was evaporated at 70° and removed immediately upon drying. The results just cited emphasize the influence of heat on lime requirement. Also when evaporation of the treated soils were conducted in the vacuum oven, the temperature appeared to be a controlling factor. At 60° in vacuo, when it required between six and seven hours to complete evaporation, the lime requirement was 1700 pounds. Any increase either in temperature or time permitted to remain in the oven after complete dehydration of treated soil further increased the lime requirement. These results show that heating at a lower temperature than 100°, namely at 60° or 75°, after evaporation has been completed, also influences the results similarly to those obtained on the steam bath where the soil was allowed to remain a short time after drying. Attention is called to the high lime requirement indicated when evaporation was conducted on the sand bath. The temperature of the sand in the sand bath varied from 70°, on the surface, to 110°, 1.5 inches below the surface proximate to the steam coil. As shown in the table it required about 8 hours to complete evaporation. This is due, probably, to the small amount of surface of the dish contiguous to the source of heat. Care was not taken to remove dishes on the sand bath immediately after dehydration and the dried soil may have been heated 15 minutes or more. If continued heating of the dried soil increases the amount of calcium hydroxide taken up, these higher results would be expected.

No difficulty was experienced in obtaining consistent results for each determination under the conditions described. Duplicate determinations gave very close results, provided the source of heat, temperature and digestion of the treated and dried soil were identical.

The other soils varying particularly in their physical properties and degree of acidity gave similar results to those observed above. In all cases the soils were removed immediately after dehydration in order to avoid excess heating of the dried soil. Table 2 gives the lime requirement of these soils when evaporated under the different conditions indicated.

All of the soil types showed a wide variation in the lime requirement, depending upon the manner in which the treated soil was evaporated. In soil 11079 we note a difference of 5500 pounds between two methods of evaporation, while in soil 11080 there is a difference of almost 10,000 pounds. Differences of this magnitude show that the lime-water method does not give an accurate index of the actual lime requirement of an acid soil.

Examination of the results thus far reported indicate that the higher the temperature at which the dry portion of the soil is subjected during the time when the undried portion is dehydrating, the higher will be the lime requirement. The reaction that occurs during the evaporation of the treated soil is apparently influenced by the temperature at which the dried portion of the

TABLE 2

The effect of heating by various means on the lime requirement of soils

SOIL NUMBER	AMOUNT TAKEN	METHOD OF EVAPORATION	LIME REQUIREMENT ($CaCO_3$ FOR 2,000,000 POUNDS OF SOIL)
	gm.		*lbs.*
11076	10.0	Steam bath	3,200
11076	10.0	Sand bath	3,900
11076	10.0	Hot plate	5,400
11077	10.0	Steam bath	1,500
11077	10.0	Sand bath	1,700
11077	10.0	Hot plate	2,400
11079	10.0	Steam bath	10,000
11079	10.0	Sand bath	12,000
11079	10.0	Hot plate	15,500
11080	10.0	Steam bath	20,800
11080	10.0	Sand bath	24,200
11080	10.0	Hot plate	30,000

soil is subjected during the process of evaporation. It is improbable that the reaction takes place in the undried portion of the soil during evaporation, although abnormal results were obtained in vacuo at 60°, which is a very low temperature compared with the actual temperature of the mixture of soil and water evaporating on a hot-water bath at 100°. It has been observed that some soils in Oregon have a higher lime requirement, as indicated by our laboratory methods, in late summer than in the spring. The fact that heating the soil even at low temperatures, as in vacuo at 60°, apparently affects the amount of lime-water taken up, may explain the cause of seasonal changes in the lime requirement.

It is well known that soils undergo chemical changes when heated even at low temperatures. One of the important reactions is the increase in the water-soluble constituents. Under the influence of heat both mineral and

organic constituents of the soil are rendered more soluble. Furthermore, it has been found that the soluble material increases at higher temperatures In the presence of moisture or water the organic material is still further transformed into the soluble state. Under these conditions, therefore, it is probable that the reaction between the soluble salts and calcium hydroxide would be increased. Also, more calcium hydroxide would probably be absorbed by a soil made deficient in bases by increased solubility of its mineral and organic constituents. Consequently, under these circumstances a soil would show a higher lime requirement by the lime-water method, depending upon chemical changes caused by heating.

Other investigators have observed several factors that affect the lime requirement of the soil as judged by the Veitch method. Brown and Johnson (1) found that grinding a soil decreased its apparent acidity, especially with coarse sandy soils. They stated that grinding to a fine powder facilitated solution and hydrolyzation of minerals contained in the soil, giving increased basicity. This was in accordance with the view held by the Rogers Brothers (4) who showed that many of the common minerals, particularly the zeolites and feldspars, when reduced to fine powder and treated with water, gave an alkaline reaction with phenolphthalein indicator. Conner (2) found that keeping soils at different moisture contents alters their acidity. Noyes (3) reported that a soil containing residual limestone gave an acid reaction to the Hopkins method, but when treated with water and evaporated on a steam bath it gave an alkaline reaction. Veitch (6) in a critical study of his lime-water method, noticed that two of the soils studied were more acid when the treated soil was dried in the open air than when dried on the steam bath. He stated that he "did not have time to make further examination of these cases." It is probable that the soils referred to by Veitch contained residual limestone similar to those reported by Noyes, since they were more alkaline after being heated on a bath. Soils 11076 and 11078 gave a very alkaline reaction when several small particles of hard limerock were added and, after treatment with water, evaporated on the steam bath. All of these observations emphasize the fact that the chemical composition and physical properties of a soil have a specific effect on the amount of calcium hydroxide necessary to satisfy the apparent acidity when artifically heated.

In a critical study of his lime-water method Veitch (6) observed that when the treated and dried soil was allowed to remain in contact with water for 48 hours or more, it developed the pink color of phenolphthalein with less lime-water than if allowed to remain in contact 16 hours or less. The wide variation in the chemical composition and physical properties of the soils used in this study suggested the possibility that similar results might not be obtained. Consequently, it was thought that a study of this phase of the subject was worthy of consideration. The procedure was followed as outlined for the previous experiments but instead of shaking the treated and dried soil with water for 16 hours it was also allowed to remain in contact for 40 hours.

Table 3 gives the amount of calcium carbonate equivalent to the lime requirement of the soil allowed to remain in contact with water as indicated.

This table presents some very interesting results. All the soils showed a reduced lime requirement when permitted to remain in contact with water for longer periods of time. Furthermore, each showed that a different reaction had occurred. During the increased time for digestion soil 11076 increased in basicity so that the lime requirement was reduced over 50 per cent; soil 11080, a very acid type, was reduced only about 20 per cent; soil 11079, also a very acid type, was reduced almost 70 per cent; soil 11077 developed basicity almost to actual alkalinity after 40 hours and when the natural soil, untreated with lime-water, was allowed to remain in contact with distilled,

TABLE 3

Lime requirement of soils allowed to remain in contact with water different lengths of time

SOIL NUMBER	METHOD OF EVAPORATION	LENGTH OF TIME SHAKEN	LIME REQUIREMENT ($CaCO_3$ FOR 2,000,000 POUNDS OF SOIL)
		hours	*lbs.*
11076	Steam bath	16	3,200
11076	Steam bath	40	1,500
11077	Steam bath	16	1,500
11077	Steam bath	40	100
11077	Steam bath	64	Alkaline
11079	Steam bath	16	10,000
11079	Steam bath	40	3,400
11079	Hot plate	16	15,500
11079	Hot plate	40	5,200
11080	Steam bath	16	20,800
11080	Steam bath	40	18,100

carbon-dioxide-free water another 24 hours or a total of 64 hours it gave an alkaline reaction. It may be mentioned at this time that this soil gives a distinctly acid reaction to all other laboratory methods, both qualitative and quantitative, for the determination of soil acidity. Veitch explains that his development of basicity may be due to the slower solubility and hydrolyzation of neutral compounds that were formed by the lime-water added, or to the hydrolization of neutral compounds already in the soil. If the peculiar action of soil 11077 can be explained on this basis it is evident that the reaction between the soil and the water constituting the normal moisture content of the soil is different from the reaction between the soil and a large amount of water added, for in no case has the soil ever shown an alkaline reaction as indicated by testing a water extract of the moist soil taken from the field.

CONCLUSION

Results obtained by a study of the Veitch lime-water method for soil acidity warrant the following conclusions:

1. The lime requirement of a soil as shown by the lime-water method indicates a reaction that takes place under the conditions performed, and the results will be affected by any variation of the following factors:
   - *a.* The physical or chemical properties of the soil.
   - *b.* Probably by the ratio of amount of soil to quantity of solutions to be evaporated.
   - *c.* The temperature at which evaporation is made.
   - *d.* Continued heating after the soil has been dehydrated.
   - *e.* The length of time during which treated and dried soil remains in contact with water.
   - *f.* The source of heat, namely, steam bath, sand bath, hot plate, etc.
2. Results will be comparative when the lime-water method is used if the determinations are conducted in exactly the same manner.
3. The data presented above emphasize the necessity of controlling all influencing factors if the lime-water method is used to observe changes in a soil by comparison of results obtained at different times.

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THE MOISTURE EQUIVALENT IN RELATION TO THE MECHANICAL ANALYSIS OF SOILS

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Mechanical analysis has been used as a basis for the classification of soils for several years. This method of classification is not altogether satisfactory in many respects, but it is the only method so far devised which gives comparable results by routine methods.

Moisture equivalent is defined as the maximum percentage of moisture which a soil can retain in opposition to a centrifugal force equal to 1000 times the force of gravity. The objects of the present investigation were to determine whether or not the moisture equivalent could be used as a basis to assist in the classification of soils, and what relation, if any, existed between the moisture equivalent and the mechanical analysis.

The moisture-equivalent determinations were made according to the method of Briggs and McLane (1), on samples of soil received by the Division of Physical Investigations from the Division of Soil Survey for mechanical analysis.

The apparatus for the determination consists of a metal cylinder attached to the shaft of a vertically mounted electric motor. The motor is provided with a governor which keeps the speed within the desired limits, a speed of 2440 revolutions per minute being necessary for a centrifugal force equal to 1000 times the force of gravity. The cylinder holds 16 soil boxes which have wire gauze bottoms permitting the escape of the excess moisture. The gauze bottoms are covered with filter paper to prevent the loss of soil particles, and then the soil is placed in the boxes, a sufficient amount of soil being taken to give a packed layer approximately 1 cm. thick. Duplicate determinations are made, the duplicate samples being placed opposite to one another in the cylinder. The samples, after being placed in the boxes, are thoroughly moistened and allowed to stand in a saturated atmosphere for 24 hours, a little more water is added, and they are placed in the cylinder of the machine. The machine is run for forty minutes at the desired speed, the samples are removed, and a moisture determination made upon each one. The percentage of moisture, based upon the weight of the dry soil, is the moisture equivalent. A total of 172 duplicate determinations were made on samples from counties in various states as follows:

La Salle, La.	26
Horry, S. C.	19
Morgan, Ala.	20
Waupaca, Wis.	17
Bertie, N. C.	12
Brawley, Cal.	9
El Centro, Cal.	9
Newberry, S. C.	2
Willits, Cal.	3
Bannock, Ida.	1
Kent, Del.	1
Fort Laramie, Wyo.	2
Lubbock, Tex.	5
Adair, Iowa	4
Cheyenne, Nebr.	23
Braxton and Clay, W. Va.	2
Chenango, N. Y.	5
Aroostook, Me.	17
Total	172

In order to determine whether or not the moisture equivalent could be used as a basis of classification, the determinations were divided into classes as determined by their mechanical analysis. The results of this grouping are shown in table 1. The mean value of the determinations in each class shows

TABLE 1

Moisture equivalent of soils grouped according to soil classification

NUMBER OF SAMPLES	DESCRIPTION	MOISTURE EQUIVALENT		
		Minimum	Maximum	Mean
2	Coarse sand	2.15	7.80	4.98
3	Sand	3.00	6.55	4.77
7	Fine sand	6.65	11.35	8.50
3	Very fine sand	9.70	12.85	10.75
9	Sandy loam	8.95	14.80	12.88
47	Fine sandy loam	9.75	25.25	16.56
9	Sandy clay	15.55	34.25	22.76
24	Loam	15.40	29.15	22.29
19	Silt loam	18.25	41.25	26.75
20	Clay loam	16.35	32.90	22.29
12	Silty clay loam	19.80	29.90	26.90
17	Clay	20.85	40.20	29.25

a gradual increase, on the whole, from class to class, with the notable exception of silt loam, but the minimum and maximum determinations show considerable variation and overlapping among the various classes. From the results shown in this table it is readily seen to be impossible to base a classification upon the moisture equivalent which would be in agreement with the present classification. However, it shows the value which the moisture equivalent may have in the interpretation of the mechanical analysis.

Since there was no correlation between the classification of soil and the moisture equivalent, there remained to be determined whether any relation existed between the moisture equivalent and the mechanical analysis. Briggs and McLane, in their work with the Bureau of Soils (2), determined that such a relation existed, but in their work the moisture retentiveness of the soil under a centrifugal force of 3000 times gravity was taken as the moisture equivalent and the effect of the organic matter in the soil was included, so the formulae derived by them were not applicable to the present work.

Briggs and Shantz (3) have derived a formula for calculating the moisture equivalent from the mechanical analysis which is as follows:

$$\text{Moisture equivalent} = 0.02 \text{ sand} + 0.22 \text{ silt} + 1.05 \text{ clay} \quad (1)$$

This formula was applied to several of the samples under consideration and found to give results which were considerably higher than the observed values, due no doubt to the high coefficient for the clay.

In order to determine whether a more satisfactory equation could be derived, an observation equation for each of the 172 samples considered was made up in the following form: x (per cent of sand) + y (per cent of silt) + z (per cent of clay) = moisture equivalent (as determined by observation). These equations were then examined by the method of least squares (4) and the values of the three unknown coefficients x, y, and z, which would most nearly satisfy the 172 observed equations, were determined, as follows: $x = 0.0627$; $y = 0.2912$; $z = 0.4257$. These values substituted in the above equation give the equation

$$0.063 \text{ sand} + 0.291 \text{ silt} + 0.426 \text{ clay} = M \quad (2)$$

where M represents moisture equivalent.

The determinations were then divided into three groups, and in a like manner an equation was derived for each group.

Group A. Soils containing less than 20 per cent silt and clay:

$$0.02 \text{ sand} + 0.40 \text{ silt} + 0.53 \text{ clay} = M \quad (3)$$

This equation was based on 15 observations.

Group B. Soils containing 20 to 50 per cent silt and clay:

$$0.02 \text{ sand} + 0.35 \text{ silt} + 0.63 \text{ clay} = M \quad (4)$$

This equation was based on 65 observations.

Group C. Soils containing more than 50 per cent silt and clay.:

$$0.11 \text{ sand} + 0.27 \text{ silt} + 0.40 \text{ clay} = M \quad (5)$$

This equation was based on 92 observations.

Groups B and C were further subdivided into their respective classes and an equation derived for each class. Group A was omitted on account of the small number of observations in each class.

TABLE 2

Calculated moisture equivalent compared with observed moisture equivalent, showing relative value of equations

SAMPLE NO.	DESCRIPTION	OBSERVED MOISTURE EQUIVALENT	CALCULATED MOISTURE EQUIVALENT												MECHANICAL ANALYSIS		
			Equation No.	M	Difference	Equation No.	M	Difference	Equation No.	M	Difference	Equation No.	M	Difference	Sand	Silt	Clay
331760	Coarse sand	4.30	2	9.31	5.01	3	6.57	2.27				1	8.06	3.76	89.5	5.6	4.8
242924	Sand	4.30	2	9.38	5.08	3	6.83	2.53				1	6.15	1.85	88.5	8.4	3.2
331757	Sand	5.65	2	9.38	3.73	3	7.41	1.76				1	9.59	3.94	87.2	6.6	6.1
331718	Fine sand	7.60	2	11.10	3.50	3	9.42	1.82				1	10.85	3.25	82.4	10.8	6.5
450850	Fine sand	9.25	2	11.33	2.08	3	9.80	0.60				1	10.01	0.76	80.6	13.8	5.1
575221	Very fine sand	6.30	2	7.80	1.50	3	4.33	−1.97				1	4.44	−1.86	94.7	4.1	1.5
450872	Very fine sand	8.20	2	11.03	2.83	3	9.51	1.31				1	9.00	0.80	81.6	14.4	4.0
242925	Sandy loam	7.70	2	12.70	5.00	4	11.89	4.19	6	11.31	3.61	1	13.01	5.31	76.7	15.9	7.6
331744	Sandy loam	15.50	2	16.46	0.96	4	17.94	2.44	6	15.17	−0.33	1	21.29	5.79	64.1	21.3	14.6
331736	Fine sandy loam	14.85	2	15.68	0.83	4	17.15	2.30	7	16.72	1.87	1	16.33	1.48	60.7	31.5	7.8
234712	Fine sandy loam	16.30	2	17.07	2.17	4	18.66	2.36	7	17.61	3.33	1	20.42	4.12	60.0	27.2	12.6
272012	Fine sandy loam	17.20	2	19.37	0.77	4	22.25	5.05	7	20.53	1.31	1	24.45	7.25	51.4	32.9	15.4
331738	Fine sandy loam	18.45	2	20.23	1.78	4	24.09	5.64	7	20.81	2.36	1	30.51	12.06	52.6	24.6	22.9
234729	Sandy clay	20.60	2	21.69	1.09	4	26.99	6.39	8	29.96	9.36	1	38.34	17.74	51.6	16.4	32.1
234713	Sandy clay	27.00	2	22.52	−4.48	4	28.74	1.74	8	31.13	4.13	1	42.96	15.96	50.4	11.7	37.5
450810	Loam	17.20	2	19.46	2.26	5	20.67	3.47	9	23.69	6.49	1	22.17	4.97	49.4	38.5	12.1
234714	Loam	18.80	2	20.33	1.53	5	21.24	2.44	9	22.50	3.70	1	22.94	4.14	45.0	42.4	12.1
272002	Loam	21.25	2	22.38	1.13	5	22.93	1.68	9	21.85	0.60	1	29.64	8.39	40.2	40.4	19.0
450833	Loam	21.65	2	22.95	1.30	5	23.28	1.63	9	25.05	3.40	1	28.43	6.78	36.9	46.6	16.6
560858	Loam	23.70	2	21.18	−2.52	5	22.05	−1.65	9	22.72	−0.98	1	27.02	3.32	44.8	38.5	16.8
234730	Silt loam	17.00	2	22.84	5.84	5	22.93	5.93	10	28.27	11.27	1	23.05	6.05	32.9	57.9	9.2
331791	Silt loam	20.10	2	23.77	3.67	5	23.64	3.34	10	27.82	7.72	1	25.01	4.71	29.9	59.4	10.8
272001	Silt loam	25.25	2	23.78	−1.47	5	23.77	−1.48	10	27.44	2.19	1	28.42	3.17	32.3	51.8	15.6
450834	Clay loam	22.90	2	23.29	0.39	5	23.62	0.72	12	23.08	0.18	1	31.41	8.51	36.9	42.2	20.4

331799	Clay loam	23.95	2	25.52	1.57	5	25.41	1.46	12	21.89	− 2.06	1	37.87	13.92	31.1	41.9	26.7
272043	Clay loam	24.15	2	24.72	0.57	5	24.75	0.60	12	22.06	− 2.09	1	36.12	11.97	33.9	40.7	25.2
450806	Clay loam	30.40	2	24.92	−5.48	5	24.88	− 5.52	12	23.02	− 7.38	1	34.71	4.31	31.9	45.1	23.0
272021	Silty clay loam	25.70	2	26.04	0.34	5	25.73	0.03	13	26.13	0.43	1	35.42	9.72	27.4	50.7	22.6
331789	Silty clay loam	26.55	2	27.15	0.60	5	26.53	− 0.02	13	27.80	1.25	1	38.30	12.75	23.8	51.1	25.3
331788	Silty clay loam	29.70	2	27.60	−2.10	5	26.85	− 2.85	13	27.58	− 2.12	1	38.71	9.01	21.8	53.1	25.3
560816	Silty clay loam	29.75	2	30.75	1.00	5	28.99	− 0.76	13	27.06	− 0.69	1	42.45	12.70	7.3	64.9	26.7
234715	Clay	33.75	2	32.65	1.10	5	31.30	− 2.45	14	32.03	− 1.72	1	61.79	28.04	14.8	33.6	51.5
272018	Clay	33.95	2	29.97	−3.98	5	29.04	− 4.91	14	26.80	− 7.15	1	51.99	18.04	20.2	38.6	41.0
450858	Clay	39.35	2	29.60	−9.75	5	26.76	−12.59	14	26.44	−12.91	1	51.28	11.93	21.4	37.8	40.5
Probable error of a single determination					±2.25			± 2.53			± 3.48			±6.76			

*Average of two determinations.

Sandy loam	9 obs.	$0.05 \text{ sand} + 0.26 \text{ silt} + 0.44 \text{ clay} = M$	(6)
Fine sandy loam	47 obs.	$0.04 \text{ sand} + 0.36 \text{ silt} + 0.43 \text{ clay} = M$	(7)
Sandy clay	9 obs.	$0.12 \text{ sand} + 0.58 \text{ silt} + 0.83 \text{ clay} = M$	(8)
Loam	24 obs.	$0.31 \text{ sand} + 0.19 \text{ silt} + 0.09 \text{ clay} = M$	(9)
Silt loam	19 obs.	$0.36 \text{ sand} + 0.26 \text{ silt} + 0.15 \text{ clay} = M$	(10)
Clay loam			
(a) Surface	5 obs.	$0.04 \text{ sand} + 0.19 \text{ silt} + 0.57 \text{ clay} = M$	(11)
(b) Subsoil	15 obs.	$0.22 \text{ sand} + 0.34 \text{ silt} + 0.03 \text{ clay} = M$	(12)
Silty clay loam	12 obs.	$0.18 \text{ sand} + 0.065 \text{ silt} + 0.80 \text{ clay} = M$	(13)
Clay	17 obs.	$0.00 \text{ sand} + 0.11 \text{ silt} + 0.55 \text{ clay} = M$	(14)

In order to determine the value of these equations, 36 samples of soil were taken at random, the only considerations being that each class should be represented, and that they should be distributed as widely as possible. Two of these samples were later rejected, one because of the very high content of organic matter and the other because it puddled in the centrifuge, giving an unsatisfactory determination of the moisture equivalent.

The moisture equivalent was determined for each of the 34 samples and compared with the moisture equivalent as calculated by each of four different formulae. The results are shown in table 2. The distribution of the samples was as follows:

Black Hawk, Iowa	10
Beaufort, N. C.	6
Mahoning, Ohio	6
Canadian, Okla.	7
Yamhill, Ore.	2
Marlboro, S. C.	2
Brawley, Calif.	1
Total	34

The results shown in this table indicate that equation (2) gives values for the moisture equivalent which on the average more nearly approximate the observed values than any of the others. Equations (3), (4), and (5) give practically the same results. Equation (3) is to be preferred to equation (2) for the soils of Group A, as equation (2) tends to give high results in this particular group. In the other two groups there seems to be little difference, but equation (2) is probably to be preferred on account of the greater ease of manipulation.

For the rapid calculation of the moisture equivalent by means of equation (2) a logarithmic chart was prepared (fig. 1). The products of the percentages of sand, silt, and clay multiplied by their respective coefficients may be read directly from the chart as illustrated in the example, then the sum of the three terms is the calculated moisture equivalent. This chart gives results which are in as close agreement as those obtained by the use of an ordinary slide rule and for the purpose of rapid calculation is more convenient.

Equations (6) to (14) give results at slightly wider variance, which seems to be an anomaly as an equation which is derived for a particular class of soil should evidently give a more accurate result than one which embodies all classes. However, because of the smaller number of observations considered in the derivation of these equations the relation existing between the sand, silt and clay, and the moisture retentiveness is not established as closely as

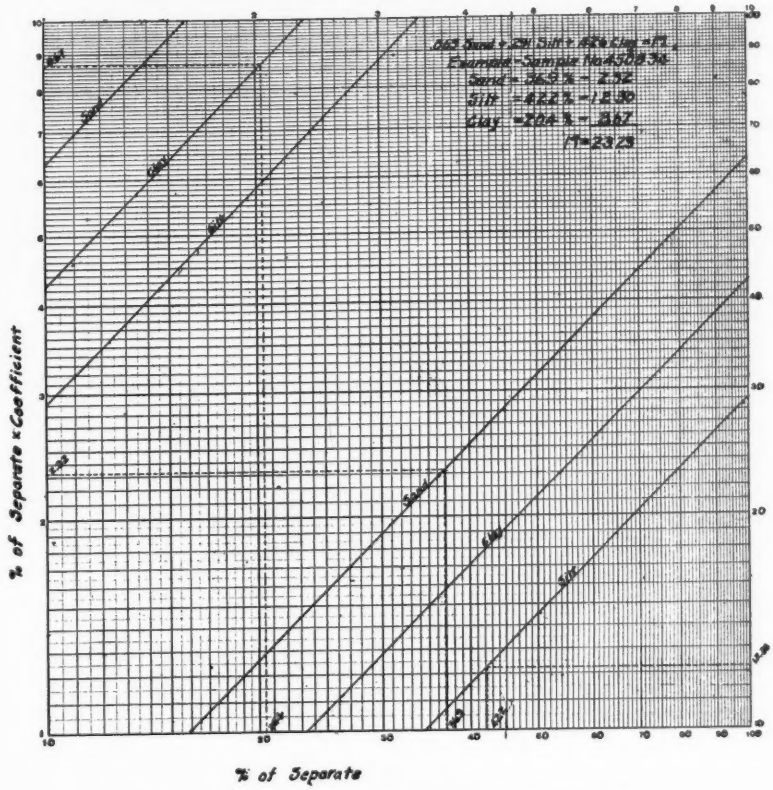

FIG. 1. LOGARITHMIC CHART FOR THE CALCULATION OF MOISTURE EQUIVALENT.

in the case where a larger number of observations are considered. This indicates also that the relation existing is practically constant in all classes of soils—differences, if any, being due to the presence of organic matter, variations in the amount of the different grades of sand, and other factors which are not taken into consideration in the application of the equations.

In order to determine the effect of a large amount of organic matter upon the moisture equivalent and to determine the relative value of the above

equations for soils of this character, determinations were made on 30 samples of soil from Traill County, North Dakota, practically all of which were high in organic matter.

TABLE 3

Observed moisture equivalent compared with calculated moisture equivalent, showing effect of organic matter

SAMPLE NUMBER	DESCRIPTION	OBSERVED MOISTURE EQUIVALENT	CALCULATED MOISTURE EQUIVALENT					
			Equation 2	Difference	Equations 3, 4, and 5	Difference	Equation 1	Difference
351701	Fine sandy loam	27.00	17.15	− 9.85	17.67	− 9.33	18.23	− 8.77
351702	Loam	23.85	23.24	− 0.61	21.13	− 2.72	25.52	1.67
351703	Loam	23.45	22.67	− 0.78	22.24	− 1.21	23.67	0.22
351704	Fine sandy loam	17.55	12.97	− 4.58	13.27	− 4.28	15.17	− 2.38
351705	Coarse sand	4.90	5.01	0.11	5.01	0.11	6.02	1.12
351713	Silt loam	33.55	26.89	− 6.66	25.23	− 8.32	28.75	− 4.80
351714	Silt loam	29.40	27.35	− 2.05	24.37	− 5.03	28.43	− 0.97
351715	Fine sandy loam	25.60	18.40	− 7.10	19.51	− 6.09	21.07	− 4.53
351716	Clay	37.55	28.84	− 8.71	28.41	− 9.14	53.36	15.81
351717	Fine sandy loam	15.05	11.26	− 3.79	10.79	− 4.26	11.48	− 3.57
351718	Fine sandy loam	25.75	18.90	− 6.85	19.26	− 6.49	18.55	− 7.20
351724	Fine sandy loam	26.80	20.36	− 6.44	22.70	− 4.10	26.69	− 0.11
351725	Sandy loam	26.35	17.26	− 9.09	21.20	− 5.15	27.44	1.09
351729	Loam	33.80	22.96	−10.84	21.78	−12.02	25.67	− 8.13
351730	Clay loam	27.90	22.25	− 5.65	23.11	− 4.79	31.62	3.72
351747	Clay loam	30.65	25.72	− 4.93	25.64	− 5.01	39.39	8.74
351748	Fine sandy loam	37.45	19.99	−17.46	21.62	−15.83	23.79	−13.66
351749	Fine sandy loam	32.85	17.52	−15.33	19.47	−13.38	22.03	−10.82
351750	Clay loam	27.30	23.16	− 4.14	23.56	− 3.74	31.69	4.39
351751	Fine sandy loam	22.35	13.63	− 8.72	13.32	− 9.03	14.01	− 8.34
351752	Fine sandy loam	18.90	13.47	− 5.43	13.27	− 5.63	15.76	− 3.14
351753	Loam	27.50	22.85	− 4.65	23.31	− 4.19	30.68	3.18
351754	Fine sand	12.70	11.32	− 1.38	9.69	− 3.01	11.46	− 1.24
351755	Fine sand	8.35	9.93	1.58	7.49	− 0.86	9.39	1.04
351756	Clay loam	34.45	24.03	−10.42	24.32	−10.13	34.55	0.10
351757	Clay loam	36.00	24.39	−11.61	24.54	−11.46	36.40	0.40
351758	Fine sandy loam	28.65	16.45	−12.20	17.83	−10.82	20.51	− 8.14
351759	Sandy clay	21.50	22.71	1.21	28.99	7.49	43.72	22.22
351760	Loam	38.20	21.26	−16.94	22.14	−16.06	28.01	−10.19
351761	Clay loam	29.50	26.37	− 3.13	26.41	− 3.09	40.67	11.17
Probable error of a single determination				± 5.65		± 5.44		± 5.32

Briggs and McLane (2) determined that organic matter has practically the same effect as an equal amount of clay in increasing the moisture equivalent. This fact is borne out in the results of the determinations as shown in table 3. In nearly every case the observed was higher than the calculated value. The results also indicate that with soils of this character the indirect determination is not as reliable as with ordinary soils, the probable error of a single

determination being approximately twice as great. It is interesting to note in this connection that equation (1), which gives results at widest variance, as shown in table 2, gave better results with soils of this character and had the least probable error. The similarity of the results of equation (2) and equations (3), (4), and (5) are borne out also, the latter in this case having a slight advantage.

SUMMARY

The moisture equivalent may not be used as a basis for the classification of soils, but may be of valuable assistance in the interpretation of the mechanical analysis.

There is a direct relationship between the miosture equivalent and the percentages of sand, silt, and clay in the soil as determined by mechanical analysis. This relation may be expressed as

$$0.063 \text{ sand} + 0.291 \text{ silt} + 0.426 \text{ clay} = \text{moisture equivalent}$$

The presence of considerable amounts of organic matter in the soil tends to increase the moisture equivalent and to disturb the relation between the moisture equivalent and the mechanical analysis.

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